$C_6H_4OH\ COO\ C_6H_5$ – Salol

Last H of Salicylic acid
is replaced

E1 9M
C. 63-97

Charles Reitman
R.I.C.P. '31

C_2H_5 ~~H_2SO_4 +~~ CH_3COOH +

9-19-30 ≡ 1-23

en zyme — in yeast (enzyme)
Pulorus - gate keeper
Chumos — juice
fundus — bottom
oiso + phein — to eat / esophagu,
de glutire — to swallow / deglutitio
Peristellein - wrap up (peristalsis)

A LABORATORY MANUAL
OF
ORGANIC CHEMISTRY

A LABORATORY MANUAL
OF
ORGANIC CHEMISTRY
FOR STUDENTS OF THE
MEDICAL SCIENCES

BY

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CHEMISTRY," "PHARMACEUTICAL LATIN."

WITH 8 ILLUSTRATIONS

PHILADELPHIA
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PREFACE

This laboratory manual of elementary organic chemistry is designed primarily to accompany the author's textbook of Organic Chemistry for Students of the Medical Sciences, but it can be used successfully with other textbooks designed for the same classes of students. It is suitable for large groups of students since very careful working directions are given, especially in the earlier experiments, in order to minimize detailed supervision and to encourage self-reliance on the part of the student. The exercises outlined are planned to occupy a minimum of four clock-hours a week for one year, but since more work is included than can usually be accomplished in that time, the instructor is free to make selections to suit individual needs.

Recent researches have proved conclusively that physicians and pharmacists must have a *broad* acquaintance with organic compounds. For this reason laboratory exercises have been selected which will bring the worker in contact with a large number of organic compounds, most of which are of medicinal interest. In addition to numerous "test-tube" experiments on a variety of compounds, the preparation of a number of compounds on a somewhat larger scale is included. Preparing type compounds in the laboratory is an excellent way of becoming acquainted not only with the particular compound that is being made, as well as others of its class, but also with the compounds which enter into the reaction, and the resulting side products. For a few important medicinals, tests for purity are given. The introductory matter which describes the laboratory operations that the student will be called upon to perform most frequently, gives important cautions, some of them seemingly very elementary, that experience in laboratory direction has shown are needed by the average student beginning organic chemistry.

The exercises have been compiled from many sources among which are: The United States Pharmacopoeia, the several textbooks of pharmacy, and a considerable number of textbooks and laboratory manuals of organic chemistry. For further and more detailed information regarding the experiments, the student is referred to such books as Adams and McElwain, *Practice of Organic Chemistry*, Barnett, *Preparation of Organic Compounds*, Cohen, *Practical Organic Chemistry*, Fisher, *Laboratory Manual of Organic Chemistry*, Fourneau, *Organic Medicaments and Their Preparation*, Gattermann, *Practical Methods of Organic Chemistry*, Norris, *Experimental Organic Chemistry*, and similar manuals.

H. C. M.

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LABORATORY MANUAL OF ORGANIC CHEMISTRY

CHAPTER I

INTRODUCTORY

1. To the Student.—To be a successful worker in organic chemistry you must:

1. Use common sense.
2. Understand what your are doing.
3. Do neat, careful, thoughtful work.

From the very beginning pains must be taken with every laboratory operation, no matter how simple it may seem. Carelessness and negligence are dangerous and inexcusable. Every student must realize that both for his own safety and for the protection of his fellow workers, a continually blundering student cannot be permitted to carry on laboratory work in organic chemistry. Blundering is most often the result of insufficient preparation before beginning work in the laboratory.

Some very valuable "laboratory work" can be done outside the laboratory. Read the working directions of each exercise through attentively, more than once if necessary, **before the laboratory work is begun.** Read any references cited. Study the textbook as well as the laboratory manual. Before you start an exercise, be able to explain to your instructor what is expected to happen during the operation, and why. Do not proceed unless you thoroughly understand what you are to do. Care in this respect will prevent the probable failure of the experiment, and possibly a serious accident. It may save hours of work.

Know the purpose of each substance used. Study the properties and actions of the interacting substances, as well as of those that result from the reaction. Remember that the compounds you are working with are usually type compounds, and that similar compounds may be expected to act in similar ways. In general one ketone acts like another ketone; one aldehyde like another aldehyde; one alcohol like another alcohol of like structure. Note particularly any action that is not true to type. Observe the special conditions used to bring about reactions.

2. The Exercise.—When the plan of work is understood, proceed to set up the necessary apparatus in a workman-like manner. A certain skill in handling and assembling apparatus is rightly expected of students who are far enough advanced to undertake the study of organic chemistry. Errors and faults that might be overlooked in a freshman course are not excused in the organic laboratory.

Follow directions carefully. Learn to distinguish between important and unimportant details. Make sure that the reacting materials are *well mixed*. Observe everything that happens during the experiment: color changes; precipitates, and their character; odors; the evolution of a gas; sublimates; separation into layers; formation of crystals; melting and boiling points, etc. Determine, if you can, the reason for the phenomena observed.

Work independently unless otherwise directed. Make notes as the work proceeds, and prepare and present your reports as the instructor directs. Be truthful. If the results obtained are not those anticipated, seek the explanation. Confer with an instructor, not with a fellow student, if you are in doubt. Do not repeat an unsuccessful experiment until the probable cause of failure has been located and corrected.

Plan your work so that your time in the laboratory is used to the best advantage. Don't rush. If an exercise calls for prolonged heating or standing, start that exercise first, at the beginning of the laboratory period. Two or more experiments may often be carried on at the same time. Keep busy. Look ahead. There is always something to be done.

3. Accident Prevention.—Guard against accidents. Keep your face away from containers which hold substances that are being heated. Protect your eyes. A flask or beaker may break without warning at any moment. Form the habit of holding the mouth of a test tube that contains reacting materials away from you. Do not look down into the test tube. Hold the tube so that any spurting material will be directed over the fingers and not into the palm of the hand. Protect your neighbor as well as yourself.

Shake liquids while they are being heated in test tubes, in order to facilitate the escape of steam or vapor. There is a difference between shaking the *tube* and shaking the *liquid* in the tube. Heat the upper portion of the liquid in a test tube first, and gradually work down so that the bottom of the tube is heated last. Reversing the process may cause spurting.

Add oxidizing agents cautiously in order to avoid sudden violent reactions. Observe odors with the greatest caution. Do not taste substances unless directed to do so.

4. First Aid.—Report all accidents immediately to the instructor in charge. Even a slight cut should receive prompt attention. Familiarize yourself with the contents of the first-aid cabinet. Apply mercurochrome or tincture of iodine to cuts, and cover with a sterile dressing. Burns caused by heat are treated at once with carron oil. Acid burns are flushed with much water immediately, and carron oil is then applied. If acid spatters in the eye, quickly flush with water, and then bathe with a solution of sodium bicarbonate. A stronger alkali must not be used. Alkali in the eye is first removed by washing with water. The eye is then bathed with a saturated solution of boric acid. A drop of olive oil in the eye will allay any subsequent irritation.

5. Fire.—There is always danger of fire in a laboratory that is devoted to organic chemistry since so many of the materials used are highly inflammable and give off inflammable vapors even at ordinary temperatures. The spilling of such substances through the breaking of apparatus, or the boiling over of a reaction mixture, or through other carelessness may result disastrously.

Take every precaution to prevent fires. Extinguish all gas flames within a radius of 12–15 feet when working with highly inflammable liquids. Use a hot water or steam bath for heating very volatile liquids which have inflammable vapors. If an open flame must be used, fit the flask with a reflux condenser. Do not allow liquids which give off inflammable vapors to stand in an open vessel near a flame. Use a wire gauze or asbestos pad when heating flasks or beakers with a gas flame. Heating cracked glass vessels is always dangerous. Glass apparatus should be dry on the outside before it is placed in the gas flame. Do not heat liquids in closely stoppered vessels.

In case of fire turn out all nearby gas flames. Smother the fire with sand or a wet cloth. Do not use water if an immiscible liquid, such as benzine, is burning. Water only spreads such a fire. Smother it with sand or dry sodium bicarbonate. Use the Pyrene extinguisher if necessary. A liquid burning in a beaker or other open vessel can be smothered with a piece of cardboard or asbestos pad. Extinguish burning clothing by smothering with a blanket.

6. Handling Materials.—Use especial care in handling such substances as bromine, phenol, phosphorus trichloride, sodium, acetic anhydride, hot concentrated acids, etc. Do not handle sticks of potassium or sodium hydroxide with the fingers. Use common sense in the disposal of waste material. Inflammable liquids must not be poured into the waste jars.

To make sure that only the specified materials will be used, read the labels on all containers *at least three times:* once, when you pick up the container; again, when you remove the material; and once again, as you put the container back in its place. Use only the amounts specified. Weighings need be accurate only to the first decimal place. Because of the danger of contaminating the main supply, do not put back an unused chemical into the container from which it was removed. Pour out only what you need.

Keep your desk top clean and dry, and the interior of your locker in a neat and orderly condition.

7. Cleaning and Drying Apparatus.—Cleanliness of all apparatus, inside and out, is imperative. Organic materials not removed by soap or scouring powder can be removed from flasks and beakers by using alcohol, benzine, chloroform, or other organic solvent. Acids often remove residues quickly. Hydrochloric acid readily dissolves the residue left when potassium permanganate has been used as an oxidizer. Commercial sulphuric acid that contains sodium or potassium dichromate makes an excellent cleanser.

After cleaning, rinse the apparatus thoroughly and set aside to drain and dry. When the apparatus must be used immediately, rinse with alcohol and then with ether. The intermediate use of alcohol is necessary because ether and water are immiscible. Ether is used for the final rinsing because of its quick volatilization at room temperature. If the apparatus is inverted and stood with its open mouth downward, the heavy ether vapor will escape. Compressed air will drive the ether out at once, or it may be drawn out with an aspirator. The breath should not be blown into a flask in an endeavor to dry it quickly. Moisture is thereby introduced rather than removed. Drying a wet flask in a flame usually breaks the flask.

Never store dirty apparatus in your locker.

8. Setting up Apparatus.—See that the apparatus you are to use is sparkling clean and set up firmly and safely in a shipshape manner. The use of string, cloth, paper, paraffin, and other like materials to seal or to hold apparatus together is not permissible. Stoppers must fit tightly. Rubber-tube connections must not be twisted nor kinked. As little as possible of the rubber should be exposed to the action of chemicals. Glass tubing should have rounded bends, without buckles, and its ends should be fire-polished. Flasks and condensers must be firmly supported and well clamped. Allowance must be made, however, for the expansion of glass when heated.

9. Stoppers.—Rubber stoppers may be used where they will not come in contact with destructive substances. If bored in the laboratory, wetting the borer and stopper with a solution of caustic alkali will aid the student to get a good channel. When inserting a glass rod or tube into the opening, moisten both the channel in the stopper and the glass tube with water or sodium hydroxide solution. Grasp the tube at a point near the end which is to be inserted, and slowly twist the tube through the opening, using as little force as possible.

Corks, before being bored, should be softened in a cork press. Then, while the cork is held in the hand, a sharp borer, one having a diameter slightly smaller than that of the desired opening, is forced with a twisting motion into the narrow end of the cork until the borer is about half way through. The boring is then started from the wider end of the cork, the two holes meeting at the center. A rat-tail file will smooth or enlarge the opening. Sealing wax or paraffin is not to be used in an endeavor to make a tight connection. Bore a new cork if necessary.

Glass stoppers and stop-cocks are ground to fit one certain opening, and each must be kept in its proper place. A piece of apparatus may be useless if its glass stop-cock is lost or broken. Take especial care with the stop-cocks of separatory funnels. A thin coating of petrolatum, or better, of a mixture of petrolatum and beeswax, will prevent glass stoppers and stop-cocks from sticking.

10. Temperature Control.—Since many organic compounds are decomposed by even moderate heat, and since in some cases excessive heat may bring about secondary reactions between the products of the reaction and the reacting substances, the constant use of a thermometer is necessary in order to control temperatures with exactness. The mere difference of a few degrees in the temperature at which a reaction is conducted may bring about the production of an entirely different substance than the one desired.

In distilling, and in determining boiling points, the thermometer bulb is not immersed in the boiling liquid; only the vapor touches it. In certain other operations in which the temperature of the reaction mixture itself is to be controlled, the thermometer is put directly into the liquid, but its bulb must not be in direct contact with the container. (Why?) Cooling a hot thermometer under a cold water tap is a good way of breaking the thermometer.

The use of a water bath or a simple steam bath insures a temperature close to, but below 100°. Temperatures further below 100° can be controlled by placing the thermometer and reaction flask directly into the water of the water bath, the temperature of the water being held at the desired point. Baths of paraffin, cottonseed oil, or concentrated sulphuric acid may be used for obtaining steady temperatures above 100°.

Final Review

Fini

When it is necessary to control reactions by cooling, flowing cold water over the container is often sufficient. If a lower temperature is required, the container is packed in snow or cracked ice mixed with table salt or calcium chloride.

11. Evolution of Gases.—Reactions in which a gas is evolved are carried on in an apparatus **which has an opening to the air.** If the container is tightly stoppered, an explosion may result. In collecting a gas over water, allow the reaction to proceed sufficiently to displace all air from the generator before collecting the gas for testing. Guard against the forcing back of water into the generator by atmospheric pressure when the reaction moderates. Removing the end of the delivery tube from the water will prevent the backward flow.

When a poisonous or irritating gas is evolved in any considerable quantity, the reaction is best performed under a hood. If carried out in the open laboratory, the gas may be passed into an appropriate solvent. For a gas of acid character, such as hydrogen chloride, an alkaline solution is used as the absorbent. If the gas is of basic character, such as ammonia, an acid solution is used to neutralize it. Water alone will serve as the absorbing agent if the gas is very soluble.

12. Solution.—Heat, agitation, and fine division of the solute hasten solution. The common solvents for organic chemicals include alcohol, ether, chloroform, benzin, benzene, acetone, carbon disulphide, carbon tetrachloride, and less frequently, water. In purification processes a solvent is chosen which easily dissolves either the desired substance or the impurities, but not both. When the solvent has become saturated, the solution is removed, and a fresh portion of the solvent is added. In this way by continued application of new portions of fresh solvent, a good separation of the substance from its accompanying impurities can be made.

13. Filtration.—For quick filtration, especially when the residue is to be discarded, use a fluted filter paper. In small filtering operations if the solid material is to be removed from the paper and saved, a plain folded paper is preferred. Filter hot solutions which precipitate on cooling in a funnel that has been warmed by passing hot water through it, or in a hot-water jacketed funnel. A short stemmed funnel is less easily clogged by a deposit of crystals. In using an aspirator with an ordinary funnel and filter paper, make sure that the tip of the filter paper is reinforced. A Buchner funnel is preferred for force filtration (Fig. 1). Funnels should not be allowed to drip on the table top.

If filter paper is attacked by the material to be filtered, use asbestos or glass wool as the filtering medium.

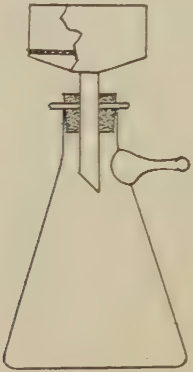

FIG. 1.

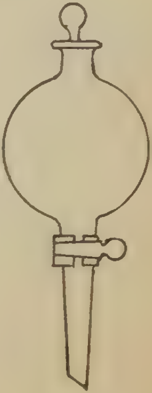

FIG. 2.

14. Extraction.—Read United States Pharmacopoeia X, pp. 452–456.

Certain precautions must be taken in using separatory funnels (Fig. 2). Place the liquid to be extracted, which should be *cool,* in the separator and add the immiscible solvent in divided portions. The total amount of the solvent to be used depends upon the amount of substance to be extracted, and its relative solubility in the two solvents. Divide the solvent into three parts in the proportion of about 60, 20, and 20 per cent. Use the largest portion first, followed by the others in turn. Add the first portion of the solvent, stopper and invert the separator, and shake the mixture with a swirling motion for several minutes so that the two liquids are thoroughly mixed. If the shaking is too violent an emulsion will result, and a sharp separation of the two liquids cannot be easily effected. While shaking, invert the separator several times to insure thorough mixing of the liquids. At intervals loosen the upper stopper to relieve any pressure that may have developed.

After the liquids have been thoroughly mixed, allow the separator to stand in an upright position until the layers separate sharply. When the separation appears to be complete, remove the upper stopper, and then if the lower liquid is to be saved, draw it off through a small filter into a second separator, flask, or beaker. Then add the second portion of fresh solvent to the liquid in the separator and repeat the whole process of mixing and separation. After the second portion is drawn off, use the third portion of the solvent, and combine the three portions of solvent that have been used.

If the upper layer in the separator is the one wanted, draw off the lower layer first and reserve or discard it as conditions may require. The upper layer can then be obtained. Remember in which layer the substance to be saved is dissolved. Time and effort are wasted if the wrong solution is discarded. If you are not certain which layer is the aqueous solution or which is the ethereal or chloroformic layer, add a little water and observe which layer is increased in volume.

Since many organic substances are less soluble in solutions of sodium chloride, calcium chloride, ammonium sulphate, and potassium hydroxide than they are in pure water, the organic compound is thrown out of solution by adding one of these compounds. Advantage is taken of this "salting out" process in obtaining a more complete separation of organic compounds from their aqueous solutions.

15. Decolorizing.—Dark-colored liquids or solutions are decolorized by heating them with activated charcoal or boneblack. The amount of the decolorizing agent to be used depends upon conditions, 1 gm. to 150–200 cc. of liquid being a reasonable amount to use as a starting point. The colored liquid is boiled with charcoal for 15–30 minutes and filtered while hot. A second or third treatment is sometimes necessary.

Undesirable color is removed from crystalline substances by recrystallization from an appropriate solvent, with or without the use of charcoal.

16. Crystallization.—The most valuable solvent to use for crystallizing operations is one in which the substance to be crystallized is very soluble when the solvent is hot, but practically insoluble when the solvent is cold. A hot saturated solution of the substance is made and allowed to cool, when crystals will be deposited because of the smaller dissolving power of the cold solvent. Solvents of low boiling points are desirable because of the quick drying of the crystals.

Crystallization from dilute solutions is brought about by concentrating the solution until crystals form readily when a small portion is cooled. The remainder of the solution is then covered lightly to protect it from dust and is allowed to stand undisturbed until a good crop of crystals is obtained. The evaporation must not be carried too far. Enough solvent must be left so that good crystals can form and there will be sufficient liquid left to keep the impurities in solution.

Crystal formation is hastened by adding a crystal of the solute, or by scratching the inside of the dish with a sharp glass rod, or by inserting strings or other foreign material upon which crystals can form. Electrolytes are sometimes "salted out" from their solutions by the addition of a second substance which contains a common ion. (Why?)

Large crystals are formed when the crystallizing solution is cooled slowly and is allowed to stand for some time without disturbing it. Quick cooling and stirring favor the formation of small crystals. The "creeping" of crystals over the edge of the crystallizing dish can be prevented by greasing the rim of the dish lightly with petrolatum.

When the crystals have been deposited, the supernatant liquid is removed by decantation, filtration, or siphoning, and the crystals are washed several times with separate portions of the cold, pure solvent. The supernatant liquid, or "mother liquor," is a saturated solution of the crystalline substance and contains most or all of the impurities that were present in the substance being crystallized. A second crop of crystals, usually less pure, can be obtained by concentrating this liquid. The crystals so obtained can be further purified by recrystallizing them from a fresh portion of the solvent.

17. Distillation.—The apparatus used for **simple distillation** consists of a distilling flask, a condenser, and a receiver (Fig. 3).

The distilling flask. The common form of distilling flask has a round bottom and a long narrow neck with a small exit tube inserted at an acute angle into the side of the neck. The flask is closed with a cork or rubber stopper containing one or more perforations through which a dropping funnel, a thermometer, or other apparatus can be inserted. The thermometer is so placed that its bulb lies just below the opening of the side exit tube, but does not reach into the liquid being distilled. The end of the dropping funnel is usually at or just below the surface of the liquid.

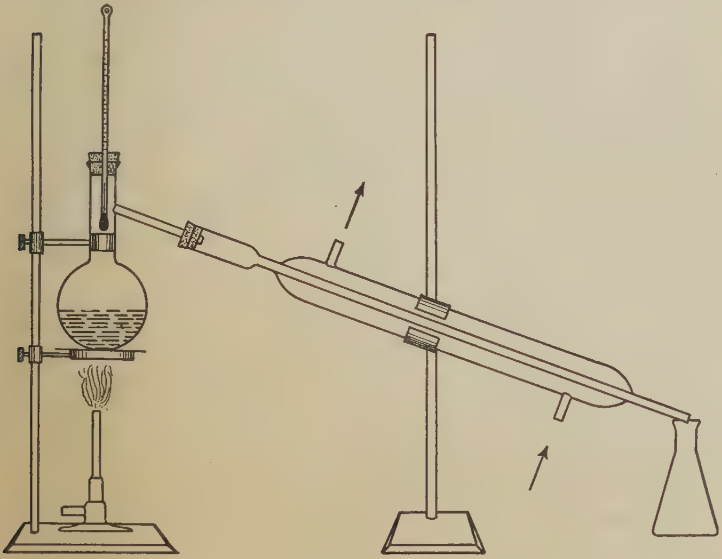

Fig. 3.

The flask is firmly supported on a wire gauze, asbestos pad, sand bath, or water bath as may be directed. To heat the flask directly, a small flame is kept constantly moving so as to avoid local overheating and bumping. Glass beads, broken tile, pieces of pumice, or an ebullition tube may be used to lessen bumping. Do not permit the liquid in the flask to boil over into the condenser. Fill the flask not more than one-half, or at most two-thirds full, in beginning the distillation. Do not hurry. If heated too rapidly, all the vapor given off will not be condensed and the yield will be lessened. A drop of distillate every 1–2 seconds is a good rate for most distillations.

Use a long-stemmed funnel for introducing liquids into the flask, and hold the flask so that the liquid cannot flow out the exit tube. Put solid substances into the flask before liquids so that the solid material will not cling to the wet neck of the flask, or else introduce the solids directly into the bulb of the flask through a funnel-like arrangement made of a piece of paper rolled into a cornucopia. ("HORN OF PLENTY")

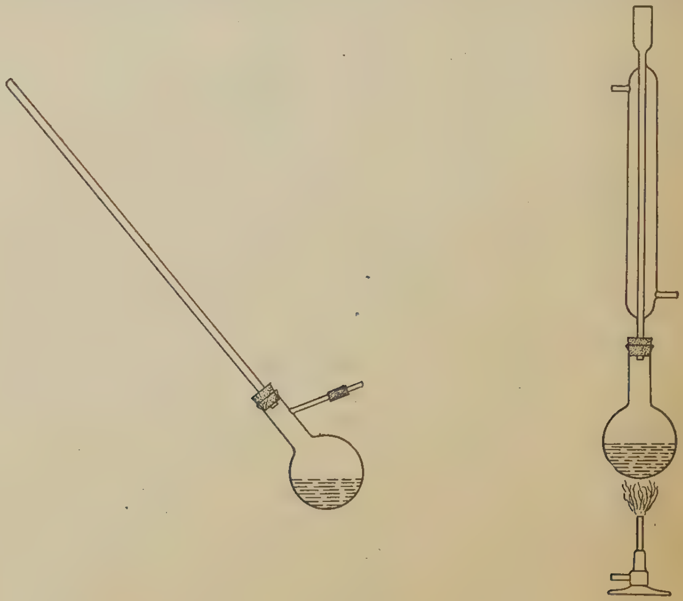

FIG. 4.

The condenser. Use a stopper to connect the side-arm of the flask to the condenser. Set the condenser horizontally, but so inclined that the condensed liquid will run off readily. Pass a

HORNED SHAPED RECEPTACLE

stream of water through the condenser jacket, having the water enter at the end nearest the *receiver*. The water outlet should be on the upper side of the condenser. Use a long condenser and a more rapid stream of water if the substance to be condensed has a low boiling point. A spiral condenser set in a vertical position provides a large condensing surface in a small space.

With substances boiling at 150° or above, a water condenser should not be used, for the high temperature on the inside and the low temperature on the outside will result in a broken condenser tube. In such cases an **air condenser,** which is merely a glass tube of fairly wide bore like the inner tube of a water condenser, is used. The relatively cold air surrounding the tube acts as a satisfactory cooling medium (Fig. 4).

When it is necessary to heat a reaction mixture for some time, or when it is desired to secure prolonged contact at ordinary temperatures without loss of a volatile ingredient, a **reflux** (flowing back) **condenser** is connected to the flask in an upright position so that a vaporous substance passing into the condenser will be condensed and flow back into the flask (Fig. 4). A reflux condenser is merely an ordinary condenser placed in a vertical position. A long air condenser may be used in this way for substances of moderately high boiling points. If the apparatus is to stand for some time at room temperature, a calcium chloride tube is placed in the top of the condenser to absorb water vapor (Fig. 5).

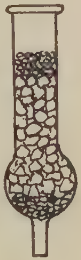
FIG. 5.

The receiver. Erlenmeyer flasks make good receivers for ordinary distillations. Place the delivery end of the condenser so that the distillate drops directly into the receiver through only a short distance. Ordinarily a connection between the condenser and receiver is not used. The receiver rests on the table top; not on a pile of books, an upturned beaker, or other piece of apparatus. If the condensed liquid is quite volatile, pack the receiver in ice or snow, or run cold tap water over it in a rapid stream. If the distillate is a heavy, volatile, immiscible liquid such as chloroform, place a small amount of water in the receiver in order to cover the distillate and thus reduce loss through evaporation.

The end of the condenser is placed under the surface of the water, and care is taken to prevent the flowing back of the water through the condenser as the pressure in the distilling flask lessens toward the end of the distillation, or varies with a change in the intensity of heating.

If the distillate is exceedingly volatile or if it must be protected from moisture, use a force filter flask as a receiver. Connect the filter flask tightly to the condenser, and fit the side outlet with a loosely packed calcium chloride tube if moisture is to be eliminated, or with a rubber tube long enough to reach nearly to the floor if ether or other substance having a heavy and inflammable vapor is to be collected. In every case make sure that there is a free opening to the air *somewhere* in the apparatus train.

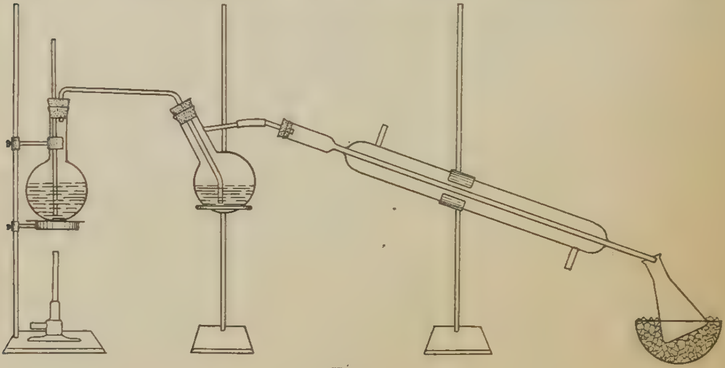

FIG. 6.

After heating has once begun, do not disconnect a distilling apparatus unless heat has been removed and the material in the distilling flask has been permitted to cool. (Why?)

In **fractional distillation** the receiver is changed when the temperature of the vapor as it distils from the flask reaches certain predetermined points. The "fractions" in the separate receivers may be redistilled.

In **steam distillation** a rapid current of steam is passed through a reaction mixture in order to take out the substance desired. This substance is condensed along with the steam in a condenser in the usual way. A second flask, tin can, or ordinary gallon metal kerosene can is used for generating the steam. A safety tube reaching nearly to the bottom is inserted through the stopper of the generator (Fig. 6).

At the beginning of the distillation care should be taken to prevent the clogging of the steam tube by any solid material that may be in the reaction flask. If the steam once starts to come over freely, stoppage is not likely to occur.

18. Drying.—To dry **solids,** spread the material in a thin layer between filter papers *on a glass plate*, and dry at room temperature, in a desiccator, over a water bath, or in a drying closet at a specified temperature. Paper holding a moist substance must not come in contact with a table top or radiator, for contamination is certain to result. Always keep a glass plate or a dish of some kind under the paper until the material is dry. Avoid contact with a metal spatula while the substance is moist. Materials being dried should be protected from dust.

Liquids are dried by allowing them to stand for some time in contact with a water-absorbing substance with which the liquid does not react. Anhydrous calcium chloride is a valuable dehydrator. It is not used for drying amines, or phenols, or other hydroxyl-containing compounds with which it reacts. Put the liquid to be dried in a flask or bottle and add a few small pieces (not powder) of fused calcium chloride. Stopper, and allow to stand with occasional shaking for an hour or two. When dried, the liquid should be sparkling and clear, and the calcium chloride should not be soggy. If the calcium chloride is water-soaked and the liquid is cloudy after standing, remove the drying agent and add fresh calcium chloride. Allow the mixture to stand for some time longer. Do not use any more drying agent than is really necessary. Too much drying agent will cause a loss of the material being dried.

Solid sodium and potassium hydroxides, and anhydrous sodium carbonate are used for drying basic substances. Alkalies cannot be used to dry acids, phenols, esters, or other compounds with which they react. Anhydrous sodium sulphate, anhydrous copper sulphate, and lime are good dehydrators for special uses.

A **gas** is dried by passing it through concentrated sulphuric acid, or over calcium chloride, lime, solid sodium or potassium hydroxides, or other dehydrating agent with which the gas does not react.

19. Changing Weight to Volume.—A simple mathematical calculation can be used to avoid the weighing of liquids if the specific gravity* of the liquid is known. A general rule for changing the weight of liquids to volume may be stated: *Divide the required weight in grams by the specific gravity of the liquid to obtain the volume, expressed in cubic centimeters, that is required.*

If the specific gravity of a liquid is 1.5, that liquid is 1.5 times as heavy as water, and every cubic centimeter of it weighs 1.5 grams. If 30 gm. of this liquid is wanted, it is evident that this amount can be had by measuring 20 cc. of the liquid.

$$\left(\frac{30}{1.5} = 20\right)$$

20. Percentage Yield.—To calculate the percentage yield of any product: 1. Weigh the amount of substance actually obtained. 2. Calculate the amount that could theoretically have been obtained from the amount of materials used. 3. Compare the two. Thus:

$$\frac{(\text{Weight obtained}) \times 100}{(\text{Weight possible in theory})} = \text{Percentage yield.}$$

In determining the amount that could be obtained theoretically, any of the reacting substances may be made the basis of the calculation, but the calculation is commonly made from the most expensive ingredient. Since the reacting substances are not always used in stoichiometrical proportions, (Why?) the final results may be quite different depending upon which ingredient is used as the basis of the calculation. In expressing the percentage yield, **the basis of the calculation should always be specified.**

An example will illustrate:

In manufacturing a lot of ethyl bromide, 20 gm. of alcohol, (92 per cent); 40 gm. of sulphuric acid, (94 per cent); and 40 gm. of sodium bromide, (98.5

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* The specific gravity of any liquid made use of in the exercises in this Manual can be learned by consulting the *Handbook of Chemistry and Physics*, Chemical Rubber Company; *The Chemist's Year-book*, Atack, or other similar books. The *United States Pharmacopoeia, X* gives the specific gravities of many important substances.

per cent) were used. 30 gm. of pure ethyl bromide was actually obtained. Calculate the percentage yield.

The amounts of ingredients actually used:

20 × 92 per cent = 18.4 gm. of alcohol.
40 × 98.5 per cent = 39.4 gm. of potassium bromide.
40 × 94 per cent = 37.6 gm. of sulphuric acid.

The following equation represents the reaction of manufacture:

$$2C_2H_5OH + 2KBr + H_2SO_4 \rightarrow 2C_2H_5Br + K_2SO_4 + 2H_2O$$

Reacting proportions——→92.12 + 238.04 + 98.08 = 217.95 + 174.26 + 36.031
Amounts actually used.——→18.4 39.4 37.6 30 (Gm. obtained)

$$\frac{217.95 \times 18.4}{92.12} = X$$

X = 43.53 gm., the amount of ethyl bromide that could theoretically be obtained from the amount of *alcohol* used.

30 gm. of ethyl bromide was actually obtained.

Then: $\frac{30 \times 100}{43.53} = 68.9$ per cent. Percentage yield on the *alcohol* basis.

A similar calculation based on the amount of potassium bromide used will show a percentage yield of 83.1 per cent. Although the results of the calculations differ widely, both are correct. Either is acceptable if the basis of calculation is specified. In this particular experiment the calculation would ordinarily be based on the amount of potassium bromide used since that is the most expensive ingredient.

21. Reagents.—Some of the special reagents and test solutions (abbreviated, T.S.) used in this Manual are described in the Appendix. The strength and purity of most of these, and of others also, will be found in the *United States Pharmacopoeia, X*, pp. 470–493.

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CHAPTER II

GENERAL PROCESSES

22. Determination of Melting Points.—(Text, p. 19. Man. pp. 3, 6. United States Pharmacopoeia, X, pp. 445–447.)*

Make several capillary (*capillus*, a hair) tubes by heating a piece of glass tubing of small bore in the flame of a Bunsen burner that has been fitted with a wing tip, until the glass has become softened. Remove from the flame and quickly pull the glass out into a long tube of very small diameter (about 1 mm.). Cut with a file into sections about 8 cm. long. Close one end of each section by holding it for a moment in the flame. Make six or more tubes. Save those not used for later experiments.

If necessary, dry the substance to be tested in a desiccator over sulphuric acid. Then grind in a mortar to a fine powder. Press the open end of a capillary tube into the powder several times until a layer of material about 1 cm. deep is obtained when the tube is held upright, and the powder is shaken to the bottom. Rasping the top edge of the tube with a file, and tapping the bottom of the tube gently on the hand or table top will make the powder settle to the bottom in an unbroken column. Fasten the capillary tube to a thermometer with a rubber band in such a way that the material in the capillary is opposite the bulb of the thermometer.

Half fill a small beaker with water, if the sample is believed to have a melting point below 100°, or with concentrated sulphuric acid or cottonseed oil if it melts at a higher temperature. Insert the thermometer and attached capillary in the liquid, and fasten the thermometer in such a way that the readings can be taken easily, and the material in the capillary is about 2 cm. below the surface of the bath liquid.

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* References are to pages in Muldoon's Organic Chemistry or to pages in this Manual.

Apply heat slowly while stirring the liquid constantly with a bent glass rod. Adjust the heat so that the rise in temperature will be about 3°–5° per minute. Watch the sample constantly and note the temperature at which the substance first appears to collapse against the side of the tube, and again when it appears to be in clear fusion. This range is the approximate melting point.

Make a second determination using a new capillary tube and another portion of the sample. Use the same bath, after cooling it some 15°–20° below the temperature at which the substance was found to melt in the preliminary test. The first heating of the second determination may proceed at an increase of 3°–5° per minute, but the rise in temperature must be very gradual, not more than 0.5° per minute, when approaching the melting point as previously determined. Stir the bath constantly. The temperature at which definite fusing occurs is taken as the melting point. Observe not only the temperature, but also the manner of melting. The gradual softening of a crystalline substance, instead of a sharp melting at a definite temperature, is an indication of the presence of impurities.

1. Report the melting point of the sample furnished.

NOTE.—In more accurate work the thermometer must be carefully calibrated, and correction must be made for the emergent stem of the thermometer, that is for the mercury in the thermometer that is not immersed in the bath liquid but lies between the surface of the liquid and the graduation on the thermometer indicating the melting point of the solid. The method outlined above can be modified for use in determining the melting points of fats and substances of similar nature.

Caution.—If concentrated sulphuric acid is used as the bath liquid, be careful not to spill it or to allow it to come in contact with the skin or clothing. Concentrated sulphuric acid is corrosive and dangerous; hot concentrated sulphuric acid is worse. Do not stir so vigorously that the stirring rod punctures the beaker. Do not allow the rubber band which holds the capillary to the thermometer to come in contact with the acid. Adding a very small crystal of potassium nitrate will clear up the dark color of the acid if it has been darkened by the presence of organic matter. Do not put hot sulphuric acid into a cold bottle after you have finished the exercise. Allow the acid to cool, and then dispose of it as the instructor directs.

23. Purification by Crystallization.—(Text, p. 14. Man., p. 10.) Acetanilid containing a chloride impurity is furnished.

Dissolve 10 gm. of impure acetanilid in the smallest amount of hot water that will dissolve it. Filter if necessary. Allow the clear solution or filtrate to cool to room temperature or below, using ice or snow if convenient. As the liquid cools, the acetanilid will be deposited as glistening white crystals. Filter off the mother-liquor, and wash the crystals on the filter with separate portions of cold distilled water until 2 cc. of the last portion of the wash water show no test for chlorides when tested with nitric acid and silver nitrate T.S. Dry the crystals (Man., p. 15.)

1. Determine the melting point of the purified acetanilid. Turn in the purified crystals at the stock room.

2. By referring to tables of melting points ascertain the melting point of pure acetanilid. Does a comparison of melting points indicate that the recrystallized acetanilid is now pure?

Why was hot water used as the solvent in this exercise? Why was alcohol not used?

24. Purification by Sublimation.—Benzoic acid containing a sulphate impurity is furnished.

Place 2 gm. of impure benzoic acid in a small porcelain evaporating dish. Cover the dish with a filter paper in which 30–40 pin holes have been made. Invert a small funnel over the filter paper, making a tight connection with the evaporating dish. Apply *low* heat to the dish, increasing the heat gradually until sublimation commences. The vaporized benzoic acid passes through the holes in the paper and sublimes upon the cool sides of the funnel. Some of it may drop off the funnel on to the filter paper. Non-volatile impurities will not be vaporized, but will remain in the evaporating dish.

The funnel may be kept cool by wrapping it in a wet cloth. Take care not to carbonize the benzoic acid by overheating. Allow the apparatus to cool before removing the funnel at the end of the exercise, so that the irritating vapor of benzoic acid will not be inhaled.

Dissolve a little of the sublimed acid in 2–3 cc. of hot distilled water and test the solution for sulphates using dilute hydrochloric acid and barium chloride T.S.

1. Have the sulphates been removed?

2. Determine the melting point of the sublimed acid. Compare it with the melting point of the pure acid. Has complete purification been effected?

25. Purification by the Use of Immiscible Solvents.—(Text, p. 13. Man., p. 8. United States Parmacopoeia, X, pp. 452–456.) Quinine sulphate containing chlorides is furnished.

This exercise depends upon the differing solubilities of quinine and quinine sulphate. Quinine alkaloid is soluble in chloroform but insoluble in water; quinine sulphate is moderately soluble in water and practically insoluble in chloroform.

Dissolve 0.5 gm. of impure quinine sulphate in 25 cc. of water, adding a few drops of dilute sulphuric acid to effect complete solution. Place in a separatory funnel and drop in a piece of red litmus paper. Add 10 cc. of chloroform to the liquid in the funnel, and then add ammonium hydroxide in small portions, with shaking, until the litmus paper indicates that the reaction of the mixture is alkaline. The quinine sulphate has now become quinine alkaloid. Explain.

Stopper the funnel, invert, and rotate in such a way that the two liquids become thoroughly mixed. The chloroform dissolves the quinine alkaloid. Do not shake violently. A thorough mixing can be obtained by gentle agitation, and troublesome emulsions are not formed.

After shaking, allow the funnel to stand upright in a ring stand until there is a sharp division into two layers. Draw off the lower chloroformic layer through a filter paper into a dry beaker. Add a fresh portion of 5 cc. of chloroform to the liquid in the separator, stopper, shake as before, allow to stand, and then draw off the chloroform through the same filter into the beaker which holds the first portion of chloroformic extract. Discard the liquid in the separator. Put the combined chloroform-quinine solutions in the separator, add a piece of litmus paper, and then 10 cc. of dilute sulphuric acid. Shake well as before. Separate the acid liquid. (Remember which is the heavier liquid and do not reject the wrong layer.) Add 5 cc. more of dilute sulphuric acid to the chloroform. Shake and separate as before. Combine the acid liquids. Test a portion of the liquid for the presence of chlorides. Evaporate off the solvent and obtain quinine sulphate.

1. Has the chloride impurity been removed? If a test for chlorides is obtained, repeat the whole process of extraction, and again test for chlorides.

2. Could alcohol have been used in place of chloroform for this extraction? Could ether have been used? Explain.

26. Purification by Distillation. Fractional Distillation. Determination of Boiling Points. Determination of the Amount of Alcohol in an Aqueous-alcoholic Liquid.—(Text, pp. 15, 21. Man., p. 11.) A mixture of alcohol and water is supplied.

Note.—Have your apparatus set-up approved by an instructor before beginning the distillation.

Caution.—Alcohol vapor is highly inflammable. Be careful of flames.

Place 300 cc. of the alcohol-water mixture in a distilling flask that has been connected with a horizontal water condenser as shown in Fig. 3. Add a few pieces of pumice stone or broken tile. Insert a thermometer through the stopper of the flask in such a way that its bulb is just below the opening into the lateral exit tube, and so that temperatures between 60° and 100° can be read easily. Using a small flame apply just enough heat to keep the liquid boiling. About one drop of distillate a second is a good rate to maintain.

Catch the distillate in separate receivers as follows: In receiving flask No. 1 collect the fraction that distils up to 83°; in No. 2, up to 88°; in No. 3, up to 93°. Into No. 4 pour the residue that is left in the distilling flask after the distillate for No. 3 has been obtained. Measure and record the volume of each of the four fractions.

Note the peculiar streaked appearance of the inside of the condenser tube near the distilling flask when the distillate consists largely of alcohol at the beginning of the distillation.

Why is the thermometer bulb not placed in the liquid in the distilling flask?

Proceed to redistil as follows: Put distillate No. 1 in the flask and distil *over a water bath* until the temperature rises to 83°, collecting the distillate in a flask labeled "A." Remove the water bath, cool the flask, place distillate No. 2 in the flask and again distil over the water bath until the temperature rises to

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assignment

83°, collecting the distillate in flask A. Change the receiver when 83° is reached, and catch the distillate in flask "B." Continue to distil until 88° is reached. Cool, add fraction No. 3, and heat until 88° is again reached, receiving the distillate in flask B. At 88° change the receiver to a flask marked "C," and continue the distillation until 93° is reached. Then add fraction No. 4 to the liquid in the flask and distil until 93° is again reached. Stop the distillation at that point.

Measure and record the volumes of each of the final fractions, and of the residue left in the distilling flask. Cool the distillates to 15.6°, and determine the specific gravity of each fraction by the Westphal balance if the volume of the distillate obtained is sufficient for determination by this method.

1. By referring to tables, ascertain the percentage of alcohol by volume in each of the distillates whose specific gravity is known. Determine from its specific gravity the percentage of alcohol in the mixture supplied at the stock room. Has fractional distillation separated the alcohol from the water? How might a more complete separation be effected?

2. After determining the specific gravities, pour about 5 cc. of each fraction into an evaporating dish and apply a flame to the surface of the liquid. Arrange the distillates in the order of their inflammability.

CHAPTER III

EXAMINATION OF ORGANIC SUBSTANCES

27. Preliminary Examination.—A substance when heated may act in any of the following ways:

1. **It may volatilize or sublime, leaving no residue.**—This behavior suggests an organic substance, but by itself is not conclusive. Certain inorganic compounds volatilize completely when heated.
2. **It may burn, leaving no appreciable residue when heated strongly.**—Such a substance is probably organic. If the flame is smoky, and if a coating of carbon is deposited on a cold dish held in the flame, there is no doubt about the organic nature of the material under examination. A "burnt" odor is often to be noticed.

   Many organic substances turn black when heated, but since certain inorganic compounds leave a black metallic residue when heated, the mere production of a black color upon igniting is in itself not conclusive evidence of the presence of carbon.
3. **It may decompose or burn, leaving an appreciable residue, even when strongly heated.**—Such a substance may be both organic and inorganic; e.g. the metallic salt of an organic acid, as calcium acetate.
4. **It may be unchanged by heat.**—Such a substance is inorganic. Inorganic crystalline compounds containing water of hydration may lose water when heated, but their composition is usually not otherwise affected by moderate heat.

Why does a pure organic compound leave no appreciable residue when heated?

How can you tell whether a substance that is being heated is burning, volatilizing, or subliming?

28. Determination of the Nature of Substances by Heating.—Heat separately in a porcelain crucible or on a crucible cover about 1 gm. each of the several unknown substances supplied at the stock room (gelatin, naphthalene, anhydrous sodium carbonate, calcium acetate, alcohol, benzoic acid, hydrated copper sulphate, etc.). Apply heat gently at first, gradually increasing as necessary and continuing to heat until no further change is observed. Notice odors, changes in appearance, and the character of the residue, if any. Hold a cold porcelain dish in the flame if the material burns, or in any vapor that may be given off.

1. After careful testing, classify the substances examined as organic, inorganic, or both organic and inorganic, stating the reason for your conclusion in each case.

Why is a substance said to be "carbonized" when it turns black on heating?

Difference between carbonization + incinera

29. Qualitative Tests for Elements.—(Text, p. 25.) Individual samples for testing are supplied. Remember that negative results are just as valuable as positive results.

Carbon.—Grind together into a coarse powder 1 gm. of the *dried* sample and 5 gm. of *dry* copper oxide. Place in a *dry* test tube and cover the mixture with a layer of coarsely powdered *dry* copper oxide about 4 cm. deep. To the test tube attach a delivery tube in such a way that it leads under the surface of 10 cc. of *clear* lime water, $Ca(OH)_2$, held in another tube. Heat the layer of copper oxide first, and then gradually bring the mixture of copper oxide and sample up to a red heat.

1. Note any change in the appearance of the lime water. If a precipitate of calcium carbonate is formed in the lime water, what is proved as to the composition of the sample? Equation.

Why does the first portion of the gas which comes over have no effect on the lime water even if carbon is present in the sample?

If this experiment is not carefully performed, the sample may not become oxidized, and if it happens to be a volatile substance such as benzoic acid, it may be carried over and deposited in the lime water. Do not mistake such a deposit for a precipitate of calcium carbonate. Repeat the experiment if necessary.

$C + 2CuO \rightarrow CO_2 + 2Cu$

Hydrogen.—Note the condensation of moisture on the inside of the cool upper portion of the test tube in the carbon test just performed. The test tube and materials were perfectly dry.

1. Where did the moisture come from? What is indicated as to the composition of the sample? Equation.

Nitrogen.—Mix 1 gm. of the sample intimately with 5 gm. of soda-lime,* and heat the mixture in a test tube. Odor? Hold pieces of moistened red and blue litmus paper in the *vapor*. Effect?

1. If an ammoniacal odor is recognized, or if red litmus paper is turned blue, what is learned as to the composition of the sample? The test, if negative, is not conclusive.

Be careful not to touch the litmus paper to the inside of the test tube. Why?

The Halogens.—Make a spiral coil by winding part of a 60 cm. piece of No. 18 copper wire closely about a lead pencil, leaving a straight wire handle about 20 cm. long attached to the coil. Heat the coil in the colorless flame until no color is imparted to the flame. Then dip the hot wire into the substance to be tested, and again hold in the flame. A green or greenish-blue color imparted to the flame shows that halogens are present, the coloration being due to volatile copper-*halogen* compounds.

1. Perform the test several times on the unknown sample, and compare with the results obtained when a substance known to contain a halogen is tested. Result?

Save the copper coil for later experiments.

The presence of halogens may be confirmed by the following test. Mix 0.5 gm. of the sample with 5 gm. of fresh lime and heat strongly in a crucible for a few minutes. Dissolve a portion of the cooled residue in dilute nitric acid, filter, and test about 3 cc. of the clear filtrate for the presence of halogen ions by using silver nitrate T.S. Result?

Oxygen.—There is no simple satisfactory test for oxygen.

Sulphur and Phosphorus.—Heat strongly in a porcelain crucible a mixture of 1 gm. of the unknown substance and 5 gm. of a mixture of sodium carbonate, 1 part, and potassium nitrate, 2 parts. Cool. Extract the fused mass with 25 cc. of warm water. Filter, and divide the filtrate into two parts.

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* Soda-lime is a granular mixture of sodium hydroxide and calcium oxide.

1. Test one portion for the sulphate ion by adding dilute hydrochloric acid and barium chloride T.S. Result?

2. Test the other part of the filtrate for the phosphate ion by adding an excess of ammonium molybdate T.S. Result?

3. If either sulphates or phosphates, or both are found, what information is gained as to the composition of the original substance?

Metals.—Ignite 5 gm. of the substance to be tested at high heat in a porcelain crucible. Dissolve the residue in water, using the smallest amount of hydrochloric or nitric acid that will effect solution.

1. Test the filtered solution for the presence of the common metals by the usual methods of inorganic chemistry. Result?

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CHAPTER IV

OPEN-CHAIN HYDROCARBONS

30. Methane. Preparation.—(Text, p. 46. Man., p. 7.) In a hard glass test tube place 5 gm. of anhydrous sodium acetate and 10 gm. of soda-lime that have been thoroughly mixed.

Anhydrous sodium acetate is made from crystalline sodium acetate, $CH_3COONa.3H_2O$, by heating the hydrated salt in a porcelain dish over a small flame. At first the salt dissolves in its own water of hydration. On further heating the water is driven off, and the salt solidifies. When heated still higher, the salt fuses. The heating is stopped at the second melting. If heated too high, decomposition takes place, acetone and sodium carbonate being formed.

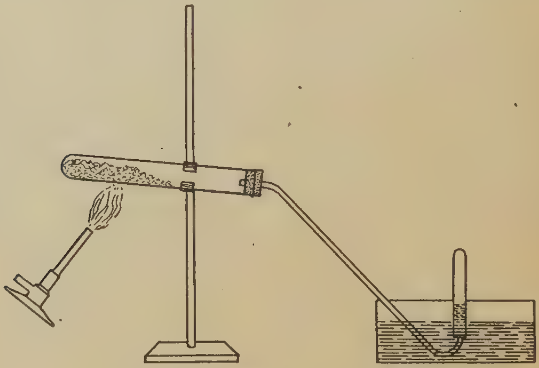

Fig. 7.

Mount the test tube on a ring stand and fit the tube with a rubber stopper and a glass tube for the collection of a gas over water as shown in Fig. 7. Have the tube inclined so that its mouth is a little lower than the closed end. This position prevents any moisture formed during the heating from flowing back

[illegible]

on the heated part of the tube, causing the tube to break. Heat the mixture in the tube with a constantly moving flame, gently at first, and then more strongly. Collect 4 tubes of the gas. Equation.

Deportment. 1. *Physical Properties.*—Observe color, odor, density, (heavier or lighter than air) and solubility in water (whether readily soluble or not).

2. *Inflammability.*—The first tubeful of gas collected is probably a mixture of methane and air. Why? Wrap the tube in a towel because of the possible danger of breaking, and hold the mouth of the tube to a gas flame. Result? In the same way light one of the tubes of gas collected later. Result? Is the gas inflammable? Does it contain carbon?

3. *Permanganate Test for Multiple Bond.**—Add about 3 cc. of a very dilute (0.01 per cent) alkaline potassium permanganate solution to a tube of the gas and shake vigorously while the tube is closed with a cork or rubber stopper. Is the permanganate solution reduced? How do you know? Is methane proved to be a saturated compound? — ? See [illegible]

[illegible]

Do not allow the permanganate solution ~~to come~~ in contact with the stopper. Why?

4. *Reaction with Bromine.*—Shake another tube of the gas with 5 cc. of bromine water. Note any color change. Explain.

5. *Interpretation.*—Have your tests proven conclusively, or merely indicated that the gas generated was methane? Explain.

31. Other Paraffin Hydrocarbons. Caution.—(Man., p. 3.) The lighter paraffin hydrocarbons are volatile and inflammable. Mixture of their vapors with air are explosive. Avoid flames.

Deportment.—Use separate portions of petroleum benzin or kerosene for the following tests.

1. *Physical Properties.*—Observe color; odor; relative density (heavier or lighter than water); effect upon litmus; solubility in

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* Do not overestimate the value of this commonly used test. Compounds containing a multiple bond are more easily oxidized than those which are saturated. The loss of color by the permanganate solution indicates that oxidation has taken place, and that the permanganate has been reduced. Even if reduction takes place, the presence of a multiple bond is not definitely proved, for any reducing agent will produce the same effect.

water, alcohol, chloroform, benzene (whether readily soluble or not).

2. *Inflammability.*—Light 2 cc. of kerosene floating on water in an evaporating dish. What information as to the composition of kerosene is gained from the appearance of the flame?

3. *Reaction with Sulphuric Acid.*—Mix 5 cc. of kerosene in a test tube with 3 cc. of pure concentrated sulphuric acid. Shake vigorously for a couple of minutes, and allow to stand until there is a good separation of the two liquids. Result?

If the kerosene contains only paraffin hydrocarbons, the two layers should be colorless. A darkening of the acid indicates the presence of hydrocarbons of some other series than the paraffin series, or possibly impurities of another nature. Do not use a cork stopper in this experiment. Why?

If a darkening in color is observed, separate the acid from the kerosene, and subsequently shake the kerosene with a new portion of acid. Upon separation, the acid should be only slightly colored, if at all, most of the impurities having been removed by the first acid treatment.

4. *Reaction with Bromine.*—To 5 cc. of kerosene add 3 cc. of bromine water and shake. Result? Explain.

5. *Permanganate Test for Multiple Bond.*—Shake 5 cc. of kerosene with 3 cc. of dilute alkaline permanganate of potassium solution. Is the permanganate reduced? What is learned?

32. Petrolatum.—(1–5). Perform the tests described under **31,** Nos. 1–5; upon separate portions of melted petrolatum and record the results.

33. Paraffin.—(1–5). Perform the tests described under **31,** Nos. 1–5, upon separate portions of melted paraffin and record the results.

6. *Reaction with Acids.*—Warm separate portions of melted paraffin with concentrated nitric acid, with concentrated hydrochloric acid, and with a concentrated solution of sodium hydroxide. Is there evidence of chemical action in any case?

34. Viscosity.—Determine roughly the relative viscosity of liquid petrolatum in the following manner. Upon a 25 cc. pipette, or one of larger capacity, make a temporary mark about 2 cm. from the delivery end. The greater the capacity of the pipette,

$C_2H_5OH + H_2SO_4 = C_2H_4 + H_2O + H_2S$

the more accurate the result will be. Fill the pipette with distilled water at 25° to the permanent graduation mark, and holding the pipette in an upright position allow the water to run unchecked into a beaker until the level of the water reaches the temporary mark on the pipette. Note and record the number of seconds that it takes the water to reach the lower level. Use a stop watch if one is available. Perform the test with water three times, and record the average of the three readings.

Dry the pipette and fill it with liquid petrolatum at 25° to the permanent graduation mark. Note the number of seconds taken for the level of the liquid to fall to the lower mark when the pipette is held as before. Perform the experiment three times, and take an average of the readings.

Divide the number of seconds taken by the petrolatum to flow from the pipette by the number of seconds taken by the water. The quotient indicates the approximate viscosity of the liquid petrolatum, water, viscosity of 1 being the standard.

35. Ethylene. Preparation.—(Text, p. 66. Man., p. 7.) Have the apparatus set-up approved by an instructor before beginning this experiment. **Caution.** Be careful of flames.

To 15 cc. of alcohol contained in a small distilling flask, add slowly with shaking 50 cc. of concentrated sulphuric acid. Keep the mixture cool. Add a few pieces of pumice, broken tile, or 5–10 gm. of clean sand, insert a thermometer through the stopper of the flask so that its bulb reaches into the mixture, and connect the exit tube of the flask with a horizontal condenser or a long glass tube arranged for the collection of a gas over water. The gas can be purified before collection by passing it through an empty wash bottle and then through a wash bottle containing a solution of sodium hydroxide. Test tubes may be used in place of wash bottles since the amount of gas to be generated is not large. The empty wash bottle or test tube is to prevent backward flow of the sodium hydroxide solution into the generating flask in case of reduced pressure in the flask. It also catches any material boiling over from the flask. Make sure that all connections are tight.

Heat the reaction mixture to 160°–175°, when there should be a good flow of the gas. Regulate the temperature so that there is

$C_2H_5COONa + Na$ [illegible]

a steady flow but not a violent reaction. Equation. Frothing may occur. Charring will probably not be entirely avoided.

After the air has been displaced from the flask collect 5 tubes of the gas. Remember that mixtures of air and ethylene are explosive. At the end of the operation extinguish the flame, and disconnect the apparatus so that there can be no backward flow into the generator.

DEPORTMENT. 1. *Physical Properties.*—Observe color; odor; density; solubility in water.

2. *Inflammability.*—Wrap a tube of the gas in a towel and light the gas. Result? Is carbon present? Verify the presence of carbon by adding 2 cc. of clear lime water to the tube immediately after the gas has been burned, and shaking thoroughly. Result?

3. *Permanganate Test for Multiple Bond.*—To a tube of gas add 3 cc. of dilute alkaline potassium permanganate solution and shake. Result? Time taken? Compare with methane? Is ethylene a saturated compound?.

4. *Reaction with Bromine.*—To a tube of gas add 5 cc. of bromine water and shake. Result? Time taken? Compare with methane. Write the graphic formula for the resulting compound. Name it.

If a small pneumatic trough was used, perform the bromine-water test upon a small portion of the water over which the ethylene was collected. Result? Is information given as to the solubility of ethylene?

36. Acetylene. PREPARATION.—(Text, p. 70.) **Caution.** Avoid flames.

Into a small **dry** distilling flask which has been fitted with an exit tube for the collection of a gas over water introduce 5 gm. of lump calcium carbide. Through the stopper of the flask insert a small dropping funnel. Drip water from the funnel drop by drop upon the carbide, and collect several tubes of gas after the air has been displaced from the flask. Equation.

It is necessary that the backward flow of water into the flask be avoided. Why is it especially important in this case? What is the residue left in the flask? What would be a safe way of disposing of the material in the flask if all of the carbide had not been acted upon by the water?

Deportment. 1. *Physical Properties.*—Observe color; odor; density; solubility in water.

2. *Inflammability.*—Wrap one of the tubes in a towel and test the inflammability of the gas. Result? Perform the same test carefully upon a mixture of acetylene and air. Result?

3. *Reaction with Bromine.*—Shake a tube of gas with 5 cc. of bromine water. Result? Time taken?

4. *Test for Multiple Bond.*—Shake a tube of acetylene with 3 cc. of dilute alkaline potassium permanganate solution. Result? Time taken? Compare with methane and ethylene. Is acetylene a saturated compound?

37. Summary.—Make a chart showing in corresponding columns the properties of the hydrocarbons of the three series studied.

COMPARISON OF OPEN-CHAIN HYDROCARBON GROUPS

H_4
H_4
$_2H_2$

Series	Color	Odor	Density	Solubility	Inflammability	Saturation
Methane						
Ethylene						
Acetylene						

Petroleum - 2, 1, 3 P. - not saponifi
kerosene

do not conta
the fatty a

and that glycerin [illegible]

CHAPTER V

HALOGEN DERIVATIVES

38. Ethyl Bromide. PREPARATION.—(Text, pp. 74, 82. Man., p. 11.) Have your apparatus set-up approved by an instructor before beginning the distillation.

To 25 gm. of ethyl alcohol (Sp. Gr. 0.78) in a distilling flask add slowly in divided portions, with shaking, 40 gm. of concentrated sulphuric acid (Sp. Gr. 1.85). Calculate the volumes of alcohol and acid required, and measure rather than weigh the quantities. Keep the acid-alcohol mixture cool by running cold tap water over the flask. To the cool mixture add carefully 20 cc. of ice water, followed by 25 gm. of finely powdered sodium bromide, taking care that the sodium bromide does not cling to the moist neck of the flask.

Arrange for distillation, using a long horizontal water condenser. Adjust the apparatus so that the delivery end of the condenser is barely covered by ice water in the receiving flask. Why? Make sure that all connections are tight. Place the distilling flask over wire gauze and heat with a small flame, gradually increasing the temperature until the ethyl bromide distils over freely. Equation.

Explain the formation of a brownish color in the distilling flask at this point.

Continue heating until no more oily-appearing drops of ethyl bromide pass over. Distil as far as possible at a uniform rate, increasing the temperature steadily so as to maintain an even pressure in the distilling flask, and so prevent a forcing back of the water from the receiver into the condenser and distilling flask.

At the end of the distillation pour off and discard the greater portion of water in the receiver. Put the rest of the water and the ethyl bromide into a separatory funnel, add 15 cc. of a 5 per cent water solution of sodium carbonate, and shake. Allow to

$Ca(OCl)_2$; $CaCl_2$

separate into two layers, draw off the ethyl bromide, and discard the alkaline solution. Wash the ethyl bromide in the separator with distilled water until the final rinsings do not affect red litmus paper.

What is the function of the sodium carbonate solution? How can the ethyl bromide layer be distinguished from the aqueous solution?

Run the ethyl bromide into a small flask or bottle, add 4–5 small pieces of fused calcium chloride, stopper and set aside for a half hour. Shake occasionally. Remove the calcium chloride if it becomes soggy, add new calcium chloride and allow the drying agent to act for some time longer. When completely dry, the ethyl bromide should be colorless and sparkling, and the pieces of calcium chloride should clink as they strike the sides of the container when it is shaken. Pour off the dry ethyl bromide and further purify it, if necessary, by distilling from a small flask, heated by hot water. Save that portion which distils between 36° and 40°.

The specific gravity of pure ethyl bromide is 1.44. Measure or weigh the amount of pure ethyl bromide obtained in this experiment. Calculate the amount that could theoretically have been obtained from the amount of sodium bromide used. What percentage yield was obtained?

DEPORTMENT. 1. *Identification.*—Observe color; odor; density; solubility; volatility; inflammability; and reaction to litmus.

2. *Halogen Test.*—Perform the copper wire test for the presence of halogens as described on page 26. Is the presence of halogens shown?

3. *Halogen Ion Test.*—To 1 cc. of ethyl bromide add 1 cc. of silver nitrate T.S. Shake. Is a bromide test obtained? Explain.

4. *Confirmatory Halogen Test.*—To 1 cc. of ethyl bromide add 5 cc. of 25 per cent sodium hydroxide solution which is free from halogen impurities. Boil the mixture until it becomes homogeneous. Equation. Cool, and test the mixture for halogen ions using dilute nitric acid and silver nitrate T.S. Result? Explain.

39. Chloroform. PREPARATION.—(Text, p. 77. Man., p. 14). Have the apparatus set-up approved by an instructor before beginning the distillation.

($C_2H_5OH + Na_2CO_3 + I_2 \rightarrow CHI_3 + NaI + CO_2$

$+3CaCl_2$

Into a distilling flask that has its side tube closed with a glass plug held in place by a piece of rubber tubing, place 100 gm. of fresh bleaching powder that has been well mixed with 250 cc. of water. Connect the flask with a reflux condenser (Fig. 4) and clamp the apparatus in an inclined position so that any liquid condensing in the side arm will flow back into the flask. Add very slowly through the condenser 15 cc. of acetone that has been mixed with 30 cc. of water. Introduce the acetone in divided portions, with shaking. If sufficient heat is not generated by chemical action to make the flask quite warm to the hand, heat the flask very gently in a water bath. Equation. Shake frequently. Allow the mixture to simmer for 25–30 minutes, but do not boil.

Remove the reflux condenser and connect with a horizontal condenser and a steam generating flask for distillation in steam. (Fig. 6.) Distil until no more oily-appearing drops of chloroform come over. Keep the receiver cool in ice water or pack it with ice or snow.

Wash the chloroform with a dilute solution of sodium hydroxide and then with distilled water until the washings are no longer alkaline to litmus. Dry over fused calcium chloride. If the chloroform is distilled from a very small flask or test tube, the portion which distils at 58°–63° should be reserved.

In this experiment the yield of chloroform, which is small, depends to a great extent upon the quality of the bleaching powder. Do not allow the steam tube to become plugged with the solid material in the reaction flask.

Deportment.—For the following tests use pure chloroform obtained at the stock room.

1. *Identification.*—Observe color; odor; taste; density; inflammability; volatility; and solubility in water, alcohol, and ether.

2. *Halogen Test.*—Apply the copper wire test for halogens. Result?

3. *Carbylamine Reaction.* **Hood.**—In a test tube under a hood, warm not more than one drop each of chloroform and aniline with 1 cc. of a 10 per cent alcoholic solution of potassium hydroxide. Equation. Note the odor *very cautiously.* Dispose of the mixture immediately as directed.

Chlorinated [illegible] acetone
[illegible]

How prep[illegible]
for anaes

This test can be used to detect a primary amine such as aniline by adding an alkali and chloroform to the mixture to be tested. The production of the foul-smelling phenylisocyanide on warming is an evidence of the presence of a primary amine.

Tests for Purity. 4. *Reaction.*—Test the reaction of chloroform with moistened red and blue litmus papers. Result?

Why might some samples of chloroform be expected to have an acid reaction?

5. *Chlorides.*—Shake 5 cc. of chloroform with 10 cc. of distilled water and allow the mixture to separate into two layers. Divide the water portion into two parts. To one portion add dilute nitric acid and 1 cc. of silver nitrate T.S. Result?

6. *Free Chlorine.*—To the other portion of the aqueous liquid add a small crystal of potassium iodide and a drop or two of starch indicator solution. Result?

7. *Impurities Decomposable by Sulphuric Acid.*—Rinse a clean glass-stoppered separatory funnel with colorless concentrated sulphuric acid. Shake 10 cc. of chloroform in the clean funnel with 3 cc. of colorless concentrated sulphuric acid. Allow to stand until the two liquids separate. The chloroform should be colorless. The acid may have only a slight color.

8. *Odorous Decomposition Products.*—Separate off the sulphuric acid in the preceding test, and dilute it with 5 cc. of distilled water. (Care.) The resulting liquid should emit but a faint vinous or ethereal odor. Result?

9. *Chlorinated Decomposition Products.*—When further diluted with 10 cc. of distilled water, the acid liquid obtained in the preceding exercise remains clear and is not affected within one minute by the addition of 3 drops of N/10 silver nitrate solution. Result?

Note.—The preceding tests for the purity of chloroform have been modified, for convenience, from the official tests of the *United States Pharmacopoeia* X. Similar modifications have been made in the tests for certain other official chemicals to be studied later. Modifications of the official tests in such a way as to make them less accurate or less sensitive would not be permissible in testing chloroform or other official substance that is to be sold or used for medicinal purposes.

10-17-30

The results of these tests should be reported as "Positive" or "Negative;" that is, the forbidden substances are "Present" or "Absent."

$C_2H_5OH + 4I_2 + 2KHCO_3 \rightarrow 2CHI_3 + 2KI + 3H_2O + 2CO_2$

40. Iodoform. PREPARATION.—(Text, p. 80.) To 10 cc. of alcohol contained in a small Erlenmeyer flask add 25 cc. of a 20 per cent solution of sodium carbonate. Place the flask in warm water and heat to 60°–70°. Then add, in divided portions, 3 gm. of powdered iodine or an equivalent amount of a water solution of iodine. Shake the contents of the flask after each addition of iodine. At the end of the operation there must be sufficient alkali left so that the solution is nearly but not completely decolorized. If necessary, add a little more sodium carbonate solution. Allow the mixture to stand for about 10 minutes at about 65°. Equation.

Cool, filter, and wash the residue with water until the washings are no longer alkaline to litmus. Dry on filter papers. Transfer to a vial and turn in at the stock room.

DEPORTMENT. 1. *Physical Properties.*—Observe color; odor; and solubility in water, alcohol, and chloroform.

2. *Microscopic Appearance.*—Make 1 cc. of a concentrated solution of iodoform in alcohol. Pour on a watch glass and allow the alcohol to evaporate. Examine the residue under a microscope, and make a sketch showing the appearance of the iodoform crystals.

3. *Halogen Test.*—Perform the copper wire test for halogens on a portion of the iodoform. Result?

41. Carbon Tetrachloride. DEPORTMENT.—(Text, p. 81.) 1. *Identification.* Observe color; odor; mobility; density; volatility; and inflammability.

2. *Solubility.*—Test the solubility of carbon tetrachloride in water, alcohol, chloroform, benzin, and cottonseed oil.

3. *Halogen Test.*—Perform the copper wire test for halogens. Result?

4. *Halogen Ion Test.*—To 2 cc. of carbon tetrachloride add 1 cc. of silver nitrate T.S. and a few drops of dilute nitric acid. Shake. Is a chloride test obtained? Explain.

40

5. *Effect on Fire.*—Set on fire a few pieces of paper in an evaporating dish. Sprinkle with 5 cc. of carbon tetrachloride. Effect? Explain.

Secondary | Ketone $>CHOH$

Tertiary $\equiv COH$

$2COH + O_2 \rightarrow CO_2 + H_2O$

21-28

Glycerin diprimary secondary alcohol

$CH_2OH.CHOH.CH_2OH$

CHAPTER VI

ALCOHOLS

42. Ethyl Alcohol. PREPARATION.—(Text, p. 95.) In a 500 cc. flask mix 25 cc. of molasses, 150 cc. of water and one-fourth of a compressed yeast cake that has been ground in a mortar with 25 cc. of water. Warm the mixture to 25°-30° *on a water bath* for 15 minutes. Shake well and put 10 cc. of the mixture in each of 3 test tubes and set them aside for observation as directed below. Note the odor of the mixture.

A solution of 25 gm. of glucose in 175 cc. of water may be used in place of the molasses. If glucose is used, add about 0.1 gm. each of potassium phosphate, calcium nitrate, magnesium sulphate, and ammonium tartrate since these compounds furnish materials that are necessary to promote the growth of yeast. The addition of this "yeast food" to molasses is not necessary, for molasses already contains the necessary elements.

After the main portion of the mixture has cooled to room temperature, close the flask with a stopper through which passes a U-shaped glass tube, the longer exit end of which is placed under the surface of some clear lime water held in a test tube or small bottle and so arranged that any gas coming from the flask must pass through the lime water. The surface of the lime water is covered with a thin layer of kerosene or light paraffin oil. Why? The other end of the U-tube should pass just through the stopper of the flask.

Record the total volume of the mixture in the flask, and set the apparatus aside in a warm place for several days.

Why allow the yeast-molasses mixture to cool to room temperature before attaching the lime-water tube?

Control of Fermentation.—Place one of the tubes holding 10 cc. of the fermentation mixture in a cold place for 24 hours or more.

Boil the mixture in the second tube for at least 5 minutes and then allow it to stand at room temperature for 24 hours or longer. To the third tube add 0.3 gm. of sodium hydrogen sulphite, $NaHSO_3$, and shake. Allow it to stand at room temperature.

At the end of 24 hours, or at the next laboratory exercise, examine the tubes and the flask containing the fermentation mixture. Is there evidence of fermentation in any of the tubes? Does it seem relatively greater or less than that observed in the flask? After making these observations, allow the tube which was kept in the cold to remain for 24 hours or longer in a *warm* place. Is there then evidence of fermentation?

1. What effect has cold on fermentation? Moderate temperature? Boiling temperature? Sulphites?

Examine the condition of the lime water in the trap attached to the fermentation flask. Result? Do not overlook any white precipitate. Explain. Note the odor of the mixture in the flask.

2. Write an equation to show the transformation of glucose, $C_6H_{12}O_6$, into alcohol and carbon dioxide.

Remove the carbon dioxide trap and allow the mixture to ferment for some time longer. Then without stirring up the yeast sediment, decant the liquid through a large filter until one-half the total amount of fermenting liquid has been obtained in a fairly clear condition. After adding sodium hydroxide T.S. until litmus paper shows a faintly alkaline reaction, put the clear liquid in a distilling flask, connect with a horizontal water condenser, and distil until exactly 50 cc. of distillate have been obtained. This distillate will contain *all* the alcohol from that portion of the fermenting liquid that is being distilled. Why?

Guard against bumping by avoiding a large excess of alkali, by careful heating, and by adding a few pieces of pumice, broken porcelain, or an ebullition tube.

3. Note the color and odor of the distillate. Pure alcohol is colorless and clear. Explain.

4. Mix the distillate thoroughly by shaking, cool to 15.6°, and determine its specific gravity by the Westphal balance. From alcohol tables ascertain the per cent of alcohol by volume in the *distillate*. Remembering that the amount of alcohol now con-

tained in 50 cc. of the distillate came from one-half the fermented liquid, calculate the percentage of alcohol by volume in the fermented liquid.

43. Identification. Iodoform Test.—(Man., p. 38.) After the specific gravity of the distillate has been taken, prove the presence of alcohol by applying the following test: Mix 10 cc. of the distillate with 4 cc. of sodium hydroxide T.S. Then add gradually in divided portions small amounts of an aqueous solution of iodine until a faint yellow color persists after shaking. Warm to 60°–70°. If a precipitate does not appear at once, set aside and examine in 10 minutes. Note the odor and the appearance of the precipitate. If a precipitate does not appear on standing, add 10 cc. more of the distillate, warm and again allow to stand, when a precipitate should appear.

The "iodoform test" is not characteristic of ethyl alcohol alone. Acetone and isopropyl alcohol respond to this test. Why was an aqueous solution of iodine specified? Why not use tincture of iodine?

44. DEPORTMENT.—Use pure 95 per cent alcohol for the following tests.

1. *Identification.*—Observe color; odor; mobility; reaction to litmus; and solubility in water, chloroform, benzene, acetone, and cottonseed oil.

2. *Volatility.*—Put a few drops of alcohol in the palm of the hand and blow upon the alcohol. Effect upon the hand? Why?

3. *Inflammability.*—Set fire to 2 cc. of alcohol in an evaporating dish. Equation. Is there evidence of the presence of carbon?

4. *Oxidation.*—To 2 cc. of alcohol add 0.5 cc. of potassium permanganate T.S. and a few drops of concentrated sulphuric acid. Heat. Result? Explain changes in color and odor.

5. *Presence of Water.*—To 10 cc. of alcohol in a test tube add 2 gm. of anhydrous copper sulphate. Stopper, shake, and allow to stand over night. Perform the same test at the same time upon a sample of dehydrated alcohol. Note any difference in the appearance of the copper sulphate in the two tubes after standing. Explain.

Make anhydrous copper sulphate by heating a portion of the hydrated salt in an evaporating dish until the water has been driven off, and the residue is grayish-white.

6. *"Salting Out."*—To a mixture of 3 cc. of alcohol and 3 cc. of water add 2–3 gm. of anhydrous potassium carbonate, and shake well. Allow the mixture to stand. Notice the separation into layers. Alcohol is "salted out" by the potassium carbonate. Which is the alcohol layer? How do you know?

7. *Reaction with Phosphorus Trichloride.*—Under a hood carefully add a few drops of phosphorus trichloride to 3 cc. of alcohol in a test tube. Equation. Guard against a vigorous reaction which may cause spattering. What are the fumes observed?

8. *Reaction with Sodium.*—To 5 cc. of alcohol in a **dry** test tube add a piece of bright metallic sodium about the size of a small pea. Equation.

Caution.—Do not handle sodium with the fingers. Keep it from contact with water. Why? Make sure that all the sodium has reacted with the alcohol before washing out the tube. Use care in disposing of any sodium not used up in this test.

9. *Formation of Ethyl Acetate.*—To a mixture of 2 cc. of alcohol and 2 cc. of water add 1 cc. of acetic acid, followed by 1 cc. of concentrated sulphuric acid. Shake and warm. Equation. Observe the odor. Carefully add a few cubic centimeters of water. Guard against spattering. Is the odor intensified by dilution?

10. *Reaction with Calcium Chloride.*—To 3 cc. of alcohol add a few small pieces of fused calcium chloride. Shake. Allow to stand. Result? Why is calcium chloride not a good drying agent for alcohol?

45. Tests for Purity. 1. *Tannin and Aldehydes.*—To 5 cc. of alcohol in a test tube add 3 cc. of sodium hydroxide T.S. Mix. Result? The liquids should not at once assume a yellow color. Any such color observed will be due to the formation of aldehyde "resins," or to the reaction with tannin which may have been absorbed from the oak cask in which the alcohol was stored.

2. *Fusel Oil Constituents.*—Mix 3 cc. of alcohol with 1 cc. of water and 0.5 cc. of glycerin. Pour the mixture on a filter paper

and allow it to evaporate spontaneously. No foreign odor should be perceptible as the last drops of the mixture evaporate. Result? Why was glycerin used?

3. *Acetone.*—To 5 cc. of alcohol add 2 cc. of sodium hydroxide T.S. and 5 drops of a freshly prepared aqueous solution of sodium nitroprusside (1 in 50). Make slightly acid with acetic acid. A violet tint, obtained within 1 minute, shows the presence of acetone. Result?

4. *Alkaloids.*—Acidulate 10 cc. of 50 per cent alcohol with 5 drops of dilute hydrochloric acid. Evaporate to about 5 cc. Dilute with water to 10 cc., filtering if there is a precipitate. Divide the liquid into two portions. To one part add a few drops of iodine T.S. To the other part add a few drops of mercuric-potassium iodide solution. The formation of a precipitate in either case indicates the presence of an alkaloid. Result?

Why is it necessary to test alcohol for the presence of alkaloids?

46. Detection of Methanol in Mixtures.—(Text, p. 101.) The common tests for detecting methanol depend upon the oxidation of methanol to formaldehyde, and the subsequent detection of the formaldehyde by various methods. The tests here given, and the other tests described under Formaldehyde, p. 49, are frequently used to determine the presence or absence of methanol in ethyl alcohol. They can be applied to *distillates* from wines, liquors, and other mixtures suspected to contain methanol. In doubtful cases always compare the result obtained on the unknown with the result of the same test made at the same time upon a solution known to contain only ethyl alcohol and upon a solution known to contain a small amount of methanol.

1. *Fuchsin Test.*—Dilute the alcoholic mixture or the distillate from a liquor until it contains about 5 per cent of alcohol by volume. To 5 cc. of this dilution add 0.5 cc. of phosphoric acid, followed by 2 cc. of a 3 per cent solution of potassium permanganate. Shake. After the mixture has stood for 10 minutes, add 1 cc. of a 10 per cent solution of oxalic acid. Shake and allow to stand until the mixture is transparent and of a brownish color. Then add in order 5 cc. of diluted and cooled sulphuric acid prepared by mixing 6 cc. of water and 2 cc. of concentrated sulphuric

acid, and 5 cc. of freshly prepared fuchsin sulphurous acid T.S. (Schiff's reagent.)

Shake and allow to stand for 10 minutes. The absence of a distinct blue or violet color on standing shows that methanol was not present in the sample in an appreciable amount. A reddish or pale green color is not significant. View the color against a white background.

How can alcohol be tested for the presence of formaldehyde?

2. *Copper Coil Test.*—Put in a test tube 10 cc. of a 10 per cent by volume solution of alcohol, or the distillate from an alcoholic mixture that has been diluted so that it now contains about 10 per cent of alcohol by volume. Heat a copper coil in the oxidizing flame until it is white hot, and then plunge it quickly to the bottom of the alcohol in the tube. Keep the alcohol cool by immersing the test tube in cold water. Withdraw the coil after a moment, and rinse it in water. Heat it again in the flame, and plunge it into the alcohol as before. Repeat the process 6–8 times. Note the odor of the vapor given off from the alcoholic liquid during the process. Equation.

Decant the liquid from the small solid particles in the bottom of the tube. This liquid now contains formaldehyde if methanol was present in the alcoholic liquid. Test for formaldehyde as follows: Add to the liquid one or two drops, not more, of a 1 per cent solution of resorcinol, and shake well. Layer this mixture over 5 cc. of concentrated sulphuric acid in a test tube without mixing the two liquids. Allow the tube to stand for a few minutes. Rotate the tube very cautiously between the hands so that a slight mixing of the two liquids is brought about. A rose-red ring, not brownish or yellow, should appear at the point of contact if methanol were present in the original liquid.

Why plunge the copper coil *quickly* to the bottom of the alcohol in the tube? Why does the copper become dull in the flame and bright in the alcohol? What are the small particles noted in the liquid after the copper coil has been used?

47. Preparation of Dehydrated Alcohol.—(Text, p. 98. Man., p. 15.) Fill a 500 cc. distilling flask one-fourth full of *pieces* of fresh unslaked lime, and introduce 250 cc. of 95 per cent alcohol. Close the side arm of the flask with a glass plug. Shake the alcohol-lime mixture well, tightly stopper the flask and allow it to stand for 48–64 hours, the longer the better. Shake the mixture several times during the standing. After 48 hours or longer, attach a horizontal water condenser, place the flask on a water bath, and distil off the alcohol. Discard the first 5–10 cc. of distillate. Collect the rest of the distillate in a perfectly dry filter flask that is fitted with a calcium chloride tube. Connect the condenser tightly to the receiving flask. Before beginning to distil make sure that there is a free opening to the air through the calcium chloride tube. Measure the amount of distillate obtained. Place in a dry bottle and stopper tightly.

Cool a portion of the distillate to 15.6° and quickly determine its specific gravity by the Westphal balance. By reference to tables ascertain its percentage strength by volume. Has the treatment with lime removed water? On a portion of the dehydrated alcohol perform the anhydrous copper sulphate test for water (p. 41). Result?

Turn in the dehydrated alcohol at the stock room. This exercise will be graded upon the amount of dehydrated alcohol obtained and upon its percentage strength.

48. "Solidified" Alcohol.—(Text, p. 95.) In an Erlenmeyer flask attached to a reflux condenser heat 60 cc. of alcohol and 4 gm. of powdered soap until a clear mixture results. Boiling for 15–25 minutes should be sufficient. Extinguish the flame. Color the solution with a few drops of phenolphthalein or methyl orange test solutions, and pour into small tin ointment jars or other containers and allow to cool, away from flames. Cover tightly to prevent evaporation. At the next exercise light a portion of the solidified mass.

49. Isoamyl Alcohol. 1. *Properties.*—Observe the color; odor; mobility; inflammability; solubility in water, chloroform, alcohol, and cottonseed oil.

2. *Formation of Isoamyl Acetate.*—To 2 cc. of isoamyl alcohol add 1 cc. of glacial acetic acid and 0.3 cc. of concentrated sulphuric acid. Warm. Note odor. Equation. The sulphuric acid acts as a catalyzer and water absorbing agent.

50. Glycerin.—(Text, p. 107.) Obtain a sample of glycerin from the stock room for the following tests:

1. *Physical Properties.*—Note general appearance; color; odor; taste; mobility; density; inflammability; reaction to litmus; and solubility in water, chloroform, alcohol, and cottonseed oil.

Caution.—Always taste chemicals cautiously, even when the identity of the substance is known. Merely touch the tongue to a small portion of the substance. DO NOT SWALLOW IT. Some chemicals can safely be tasted only when highly diluted. In this particular case, pure glycerin would be harmless, but impure glycerin might contain substances, added deliberately or otherwise, that might be very dangerous.

2. *Reaction with Potassium Bisulphate.*—Heat 0.5 cc. of glycerin with 0.5 gm. of potassium bisulphate. Acrolein, recognized by its sharp irritating odor, is given off.

3. *Borax Bead Test.*—Into a water solution of glycerin, 1–5, dip a borax bead made in the usual way on a platinum wire. Hold the moistened bead in the colorless flame and note the color imparted to the flame. Perform the test several times in order to become familiar with the identification of glycerin by this method.

A dilution 1–5 means to mix 1 part of glycerin with 4 parts of water.

Tests for Purity. 4. *Residue on Burning.*—Heat 5 gm. of glycerin in an evaporating dish until it catches fire. Allow it to burn undisturbed without further application of heat, in a place free from draughts. Not more than a very slight residue of carbonaceous and mineral matter should remain. Upon further ignition at a low red heat no appreciable residue should be left.

5. *Readily Carbonizable Impurities.*—In a clean glass-stoppered bottle or cylinder shake vigorously 5 cc. of glycerin with 5 cc. of concentrated sulphuric acid. The liquid does not become darker than yellow on standing for one hour.

6. *Oxalic Acid.*—An aqueous solution of glycerin 1–10 remains clear upon the addition of calcium chloride T.S.

7. *Sulphates.*—An aqueous solution of glycerin remains clear upon the addition of 0.5 cc. of dilute hydrochloric acid followed by the addition of barium chloride T.S.

$_3H_5(OH)_3 + KHSO_4$

$C_3H_4O + 2H_2O + KHSO_4$

8. *Acrolein. Glucose. Ammonium Compounds.*—Mix 5 cc. of glycerin with 5 cc. of a 10 per cent aqueous solution of potassium hydroxide and heat in a water bath to 60°. The mixture should not become yellow when kept at 60° for 5 minutes. (Acrolein. Glucose.) Nor should the mixture emit an odor of ammonia. (Ammonium Compounds.)

9. *Heavy Metals.*—An aqueous solution of glycerin 1–10 acidulated with hydrochloric acid does not give a colored precipitate of metallic sulphides when saturated with hydrogen sulphide. Heavy metals, such as lead, mercury, silver, bismuth, copper, arsenic, antimony, tin, etc., respond to this test.

CHAPTER VII

ETHERS. ALDEHYDES. KETONES

51. Ethyl Ether. PREPARATION. (Text, p. 114. Man., p. 14.) **Caution.**—Danger. Avoid contact of ether and ether vapor with flames. Ether vapor is heavy and very inflammable. Have the apparatus set-up approved by an instructor before beginning the experiment. Students are **forbidden** to start the ether distillation until the instructor has given permission.

Cautiously mix 25 cc. of alcohol and 25 cc. of concentrated sulphuric acid in a distilling flask. Add the acid to the alcohol in divided portions, slowly, and with shaking. Arrange for distillation using a long horizontal condenser through which a rapid stream of water is flowing. Insert a thermometer and dropping funnel through the stopper of the flask, having the ends of both reaching into the alcohol-acid mixture. For a receiving flask use a filter flask or an Erlenmeyer flask tightly connected to the condenser but having an outlet to which is attached a rubber tube long enough to reach nearly to the floor. Through this tube any ether vapor which escapes from the receiver is conducted downward and away from the flame. **There must be a free outlet to the air.** The receiving flask is packed in ice or snow.

The liquid in the flask is heated gradually up to 140°, at which point ether will distil over. Equation. When ether begins to come over, add slowly through a dropping funnel 25 cc. of alcohol, allowing the alcohol to enter at about the same rate that the ether distils. The volume of liquid in the distilling flask will then remain nearly constant. The temperature *must* be kept between 140° and 145°. It must not go above 145°.

When 40–50 cc. of distillate have been obtained, *extinguish the flame,* and disconnect the receiver. **No flames are to be within 15 ft. when the connection is broken.** Pour the distillate

$3H_2SO_4$

$CH_3OH + O \to 2H + CHO$

into a separatory funnel and shake it with an equal volume of water containing a small amount of sodium hydroxide. This treatment is to remove alcohol and sulphurous acid. Where did these come from?

Draw off the aqueous liquid and discard it. Dry the ether by allowing it to stand over calcium chloride. It may be further purified by redistillation. Turn it in at the stock room.

DEPORTMENT.—Obtain a sample of ether from the stock room for the following tests:

1. *Physical Properties.*—Observe color; odor; mobility; volatility; reaction to litmus; and solubility in water, alcohol, chloroform, benzene, and benzin.

2. *Volatility.*—Pour a few drops of ether on the hand and blow upon it. Effect on ether? Effect on hand? Explain.

3. *Inflammability.*—Place not more than 2–3 drops of ether on a watch glass and quickly apply a flame. Result? Do not have the remainder of the ether in an open vessel near the flame.

Drop *not more* than 3–4 drops of ether into an empty 500 cc. wide mouth bottle. Cover the opening with a glass plate. When the ether has evaporated, remove the plate and drop a lighted match into the bottle. Care! Result?

ALDEHYDES

52. Formaldehyde. PREPARATION.—(Text, pp. 119, 122.) To 50 cc. of a 10 per cent aqueous solution of methanol add 20 cc. of a 5 per cent solution of potassium permanganate and 1 cc. of concentrated sulphuric acid. Shake, warm, and allow to stand for 10 minutes. Equation. Filter, and use the filtrate which is an impure solution of formaldehyde for the following tests.

DEPORTMENT. 1. *Odor.*—Observe the characteristic formaldehyde odor.

2. *Tollen's Test.*—To 5 cc. of Tollen's reagent, (Appendix, p. 111) add 1 cc. of the formaldehyde solution. Warm very slightly by placing the test tube in a beaker of warm water for a few moments. A silver mirror should be formed in the test tube. Do not allow this mixture to stand for more than a few minutes.

NOTE.—The test tube in which the Tollen test is carried out should be chemically clean. If the tube is not clean, the silver will be precipitated not in the form of a mirror but as a black granular precipitate. Boiling a solution of sodium hydroxide in the tube, and then rinsing with distilled water will clean the tube thoroughly.

Caution! The mixture resulting from Tollen's test should always be washed out at once, and the test tube should be thoroughly cleaned. An explosive precipitate may form if the mixture is allowed to stand.

3. *Fuchsin Test. Schiff's Test.*—To 1 cc. of formaldehyde solution add 3 cc. of fuchsin-sulphurous acid T.S. and 1 cc. of concentrated sulphuric acid. Shake. Result? Observe whether the color is produced at once or only upon standing.

4. *Fehling's Test.* To 5 cc. of alkaline cupric tartrate T.S. (Fehling's solution) add 1 cc. of formaldehyde solution and heat to boiling. A red precipitate of cuprous oxide is formed. Has the *aldehyde* been oxidized or reduced? 1/2 - [illegible]

5. *Resorcinol Test.*—To 1 cc. of the formaldehyde solution add 2 drops of a 0.5 per cent solution of resorcinol, and layer the mixture over 4 cc. of concentrated sulphuric acid in a test tube in such a way that the two liquids do not mix. Note the rose-red coloration at the point of contact of the two liquids. A brownish or yellowish color is not significant. An excess of resorcinol is to be avoided.

6. *Milk Test.*—To 3 cc. of concentrated sulphuric acid, Sp. Gr. 1.8, in a test tube add 1 drop of a 5 per cent solution of ferric chloride. From a pipette run in about 5 cc. of milk containing a *very small* amount of formaldehyde. Do not mix the acid and milk. A violet colored zone should appear between the two liquids. This test is more sensitive when the milk is diluted, and the acid-milk mixture is warmed.

Acid of a specific gravity greater than 1.8 may give a reddish-brown ring instead of the characteristic violet color. If the brownish color is obtained, dilute the acid to make it of the required specific gravity and perform the test on a new portion of milk. This test is most sensitive when the amount of formaldehyde in the milk is small.

This test may be performed in another way. To 10 cc. of milk in an evaporating dish add 10 cc. of concentrated hydrochloric acid containing 1 drop of 5 per cent ferric chloride solution. Hold the dish over a flame, using a rotary motion to keep the mixture well stirred. If a small amount of formaldehyde is present in the milk being tested, the mixture should take on a violet color as the temperature approaches 100°.

Use a solution of formaldehyde obtained from the stock room for the following tests. Bonnet's Test

7. *Morphine Test.*—Add 3–4 drops of formaldehyde solution to 1 cc. of concentrated sulphuric acid in which a little morphine has been dissolved. An intense violet color should be observed.

8. *Reaction with Alkalies.*—Warm 2 cc. of formaldehyde solution with 2 cc. of sodium hydroxide T.S. Result? $HCOONa + CH_3OH$

9. *Reaction with Salicylic Acid.*—Add 2 drops of formaldehyde solution to 5 cc. of concentrated sulphuric acid in which about 0.02 gm. of salicylic acid has been dissolved. Warm the liquid gently. A permanent, deep red color appears.

10. *Polymerization.*—Allow 10 cc. of formaldehyde solution to stand in an open beaker for some hours exposed to the air, or slowly evaporate 10 cc. of the solution on a water bath under a hood. What is the white substance obtained? Explain. Equation.

Filter off the liquid, and dry the solid material. Ignite a small portion of it. Odor?

Perform the Tollen and Fuchsin tests for aldehydes upon small portions of the solid. Result?

11. *Action on Gelatin.*—Insert a piece of sheet gelatin in a formaldehyde solution and allow it to remain for several hours. Remove the gelatin and test its solubility in warm water. At the same time test the solubility of untreated gelatin in warm water. What is the effect of the formaldehyde treatment?

53. Acetaldehyde. PREPARATION.—(Text, pp. 119, 125.) In a distilling flask carefully mix 25 cc. of water, 15 gm. of concentrated sulphuric acid, and 10 gm. of potassium or sodium dichromate. Cool. Insert the stem of a dropping funnel through the stopper of the flask, having the end of the stem come just under the surface of the liquid in the flask. Connect the flask with a horizontal water condenser. Cool the receiver by flowing cold water over it or by packing it in ice.

Put 15 cc. of alcohol in the dropping funnel and run the alcohol *slowly* into the oxidizing mixture, a little at a time. **Shake the**

flask well after each addition of alcohol. If the liquids are not well mixed, two layers will form, and the reaction will take place violently all at once later on. Warm the flask *gently* if necessary to start the reaction. If too much heat is applied, the reaction will be difficult to control. Collect about 15 cc. of distillate. Mix it thoroughly by shaking and use separate portions of it for the following tests:

DEPORTMENT. 1. *Odor.*—Observe the characteristic odor.

2, 3, 4. *Reducing Action.*—Perform the Tollen, Schiff, and Fehling tests, Nos. 2–4 under Formaldehyde, p. 49, and record the results.

5. *Reaction with Alkalies.*—To 2 cc. of aldehyde solution add 2 cc. of sodium hydroxide T.S. Warm. Result? Compare with formaldehyde.

6. *Oxidation.*—To 5 cc. of the aldehyde solution add 0.5 cc. of concentrated sulphuric acid and 5 cc. of 10 per cent solution of potassium dichromate. Heat. Hold moist blue litmus paper in the vapor. Result? Equation.

7. *Reaction with Sodium Bisulphite.*—Shake 3 cc. of acetaldehyde, obtained from the stock room, with 5 cc. of a *saturated* solution of sodium bisulphite. Cool. Result? Write the graphic formula for the resulting compound.

2-1-30

54. Chloral Hydrate. DEPORTMENT. (Text, p. 127.) 1. *Reducing Action.*—Dissolve 1 gm. of chloral hydrate in 4 cc. of water, and divide into 2 portions. Test one part with Tollen's reagent to determine if the aldehyde group is present. Test the other with Fehling's solution. Results?

2. *Reaction with Sulphuric Acid.*—To 3 gm. of chloral hydrate crystals add 3 cc. of concentrated sulphuric acid. Warm. Observe the separation into layers. Explain. Equation.

Withdraw a few drops of the oily liquid and mix it with a few drops of water. Result? Explain.

3. *Action with Thymol.*—Rub in a dry mortar or evaporating dish a few crystals of chloral hydrate with an equal amount of thymol or gum camphor. Result?

4. *Reaction with Caustic Alkalies.*—To 1 gm. of chloral hydrate add 4 cc. of sodium hydroxide T.S. and heat. Identify the odor. Equation.

Incompatible

Alcohol formed

CCl_3 ~~CHO~~ + NaOH →
~~CCl~~ C [illegible]

Why should chloral hydrate not be dispensed in medicinal mixtures containing alkalies?

KETONES

11-21-30

$Ca(C_2H_3O_2)_2 +$
$(CH_3)_2CO + CaC$

55. Acetone. Preparation.—(Text, p. 130). In a strong glass test tube place 5 gm. of granular calcium acetate which has been thoroughly mixed with 5 gm. of anhydrous sodium acetate. Fit with a rubber stopper and bent glass tube so that the exit gases can be run into 5 cc. of water held in a test tube. Heat the acetates, gently at first and then with increased heat. An impure solution of acetone is obtained. Equation.

In writing the equation consider only the calcium acetate. The sodium acetate is added to hasten the reaction.

Deportment. 1. *Odor.*—Note the characteristic odor of the distillate. Use it in the following tests:

2, 3. *Reducing Action.*—Perform the Schiff and Tollen tests as described under Formaldehyde, p. 49. Compare the results obtained with those obtained with formaldehyde.

4. *Iodoform Test.*—Apply the iodoform test as described under Alcohol, p. 41. The iodoform test for acetone should respond at *room temperature.* Warming as in the case of alcohol is unnecessary.

Obtain acetone from the stock room for the following tests.

5. *Identification.*—Observe color; odor; mobility; density; inflammability; volatility; and solubility in water, alcohol, chloroform, and cottonseed oil.

6. *Reaction with Alkalies.*—Warm 2 cc. of acetone with 1 cc. of sodium hydroxide T.S. Result?

7. *Reaction with Sodium Bisulphite.*—Mix 3 cc. of acetone with 5 cc. of a saturated solution of sodium bisulphite. Shake well. Cool. Result? Equation.

How might the acetone be regained from the resulting compound?

8. *Oxidation.*—To a mixture of 2 cc. of acetone and 5 cc. of a 5 per cent solution of potassium dichromate add 2 cc. of concentrated sulphuric acid. Equation. Guard against spurting when mixing the liquids. Warm if necessary.

$CCl_3CHO + NaOH \rightarrow CHCl_3 + NaCOO$

9. *Reaction with Sodium Nitroprusside.*—To 3 cc. of a dilute aqueous solution of acetone add 5 drops of a freshly prepared dilute solution of sodium nitroprusside, followed by 2 cc. of sodium hydroxide T.S. A deep red color is produced upon the addition of a slight excess of acetic acid. When diluted with several volumes of water, a violet tint is developed. This test is used to detect the presence of acetone in the urine.

Summary.—Draw up in tabular form a list of the points of likeness and difference between alcohols, ethers, aldehydes, and ketones.

Spirits of ants - K.F

CHAPTER VIII

OPEN-CHAIN ACIDS

56. Formic Acid.—(Text, pp. 135, 137.) Use a solution of formic acid obtained at the stock room for the following tests. Do not allow formic acid to come in contact with the skin.

DEPORTMENT. 1. *Odor. Reaction.*—Note the odor of formic acid, and its reaction to litmus.

2. *Reducing Action.*—Neutralize 5 cc. of formic acid solution with sodium hydroxide T.S. Test 2 cc. portions of the resulting solution of sodium formate with Fehling's solution and Tollen's reagent. Results?

To the remainder of the solution of sodium formate add an equal quantity of 5 per cent solution of mercuric chloride. Warm gently. Result? What is the precipitate?

3. *Oxidation.*—To 5 cc. of formic acid solution add 2 cc. of diluted sulphuric acid and a few crystals of potassium dichromate. Shake. Warm. Pass the evolved gas into lime water. Result? Equation.

57. Acetic Acid. PREPARATION.—(Text, p. 139.) In a distilling flask mix 35 cc. of water and 20 gm. of concentrated sulphuric acid. (Care!) Add 10 gm. of potassium or sodium dichromate, and cool. Close the side-arm of the flask with a glass plug, and connect the flask to a reflux condenser. Through the condenser add slowly in divided portions, with constant shaking, 5 cc. of alcohol that has been diluted with 20 cc. of water. Heat the mixture gently on a water bath for 20 minutes, shaking occasionally. Take care to avoid a sudden violent reaction which may be caused by an imperfect mixing of the materials, or by too rapid heating. The mixture may boil up suddenly and even pass out through the condenser. After heating for 20 minutes, cool, connect the flask with a horizontal water condenser, and distil until 15–20 cc. of distillate have been obtained.

Note that the same materials are used in this exercise as in the preparation of Acetaldehyde, p. 51, but that there is a considerable difference in the relative amounts used. Is a greater or less degree of oxidation indicated by the proportions used in this exercise?

DEPORTMENT. 1. *Odor. Reaction.*—Note the odor of the distillate. Test it with litmus. Divide the distillate into several parts and use it in the following exercises.

2. *Reducing Action.*—Test the reducing action of acetic acid by using the Fehling, Tollen, and mercuric chloride tests used with formic acid. Results?

3. *Ester Formation.*—To 2 cc. of the distillate add 1 cc. of alcohol and 0.5 cc. of concentrated sulphuric acid. Warm. Note the odor. Equation. This is one of the commonly used identification tests for acetic acid.

Use glacial acetic acid in the following tests.

4. *Inflammability.*—Heat 1 cc. of glacial acetic acid to boiling in a test tube. Is the vapor inflammable?

5. *Congealing Point.*—Place 5–10 cc. of glacial acetic acid in a test tube. While constantly stirring the acid with a thermometer, slowly cool by placing the test tube in a beaker of snow or ice. Note the temperature at which congealing takes place. If pure, the acid should solidify at a temperature not below 14.5°. When only a little water is present, each per cent of water lowers the congealing point about 1.8°.

6. *Reaction with Ferric Chloride.*—Just neutralize 1 cc. of dilute acetic acid with ammonium hydroxide, and then add 0.5 cc. of a ferric chloride solution. Equation. The blood red color is discharged upon the addition of sulphuric acid.

7. *Summary.*—By what tests may acetic and formic acids be distinguished?

58. Oleic Acid. DEPORTMENT. 1. *Identification.*—Note general appearance; odor; density; solubility in water, alcohol, chloroform, and warm sodium hydroxide solution.

2. *Congealing Point.*—Determine the congealing point of oleic acid as directed under Acetic Acid, Test No. 5.

3. *Formation of Elaidic Acid.*—To 5 cc. of oleic acid add 1 gm. of sodium nitrite and a few drops of concentrated sulphuric acid.

Shake well and allow to stand. The solid isomer, elaidic acid, is formed.

59. Oxalic Acid. PREPARATION.—(Text, p. 155.) In an Erlenmeyer flask put 8 gm. of granulated sugar and 50 gm. of concentrated nitric acid. Heat on a steam bath at about 40° until the brown fumes of nitrogen tetroxide begin to come off. Quickly place the flask under a hood and allow it to stand until the evolution of fumes has practically ceased. Evaporate the remaining material on a steam bath until the liquid measures about 25 cc. Allow it to cool and stand at rest until the oxalic acid crystallizes. Filter, dissolve the crystals in the smallest amount of hot water that will dissolve them, and allow the solution to cool. Good crystals of oxalic acid should form.

DEPORTMENT. 1. *Physical Properties.*—Observe the general appearance; odor; color; and solubility in water and alcohol. Taste a small crystal very cautiously. **Do not swallow.** Oxalic acid is poisonous.

2. *Action of Heat.*—Heat 1 gm. of oxalic acid crystals in a test tube, observing carefully. The acid melts in its water of hydration at about 99°. As the heating is continued the water is driven off, and the anhydrous acid sublimes at a temperature above 150°. Is there a noticeable odor on heating?

3. *Reaction with Calcium Salts.*—To 1 cc. of a 10 per cent aqueous solution of oxalic acid add sufficient ammonium hydroxide to nearly neutralize it. Add 1 cc. of a 10 per cent calcium chloride solution. Is a precipitate formed immediately? Is heat necessary for its production? Equation.

4. *Reducing Action.*—Apply Fehling's and Tollen's tests to separate portions of an aqueous solution of oxalic acid. Results?

5. *Reaction with Cupric Hydroxide.*—To 2 cc. of a 5 per cent aqueous solution of copper sulphate add 10 cc. of sodium hydroxide T.S. Equation. Will the precipitate dissolve in a solution of oxalic acid?

6. *Reaction with Ferric Hydroxide.*—To 2 cc. of a 5 per cent solution of ferric chloride add 10 cc. of sodium hydroxide T.S. Equation. Test the solubility of the precipitate in oxalic acid. Result?

7. *Ink Removal.*—Determine the effect of oxalic acid solution on a cloth stained with a solution of ferric chloride. Result? On a cloth stained with ink? Result? Was the ink an iron ink, or one made with a coal-tar color?

60. Tartaric Acid. DEPORTMENT. (Text, p. 165.) 1. *Physical Properties.*—Observe the general appearance, odor, and taste of tartaric acid. Test its solubility in water and alcohol.

2. *Action of Heat.*—Heat 1 gm. of tartaric acid slowly in a test tube. Is a "burnt sugar" odor recognized?

3. *Reaction with Calcium Salts.*—To 1 cc. of a 10 per cent solution of tartaric acid add sufficient ammonium hydroxide to nearly neutralize it, and then add 1 cc. of a 10 per cent solution of calcium chloride. Result? Boil for 1 minute. Result? Compare with oxalic acid.

4. *Reducing Action.*—Apply the Fehling and Tollen tests to separate portions of a water solution of tartaric acid. Results?

5. *Reaction with Cupric Hydroxide.*—To 2 cc. of a 5 per cent solution of cupric sulphate add 10 cc. of sodium hydroxide T.S. Test the solubility of the precipitate in a solution of tartaric acid. Result? Why is a tartrate used in making Fehling's solution?

6. *Reaction with Ferric Hydroxide.*—To 2 cc. of a 5 per cent solution of ferric chloride add 10 cc. of sodium hydroxide T.S. Test the solubility of the precipitate in a solution of tartaric acid. Result?

7. *Potassium Salt.*—To 3 cc. of a 50 per cent solution of tartaric acid add 3 cc. of a concentrated solution of potassium acetate. Result? Equation. Test the solubility of the *precipitate* in acetic acid, hydrochloric acid, and sodium hydroxide T.S.

61. Citric Acid. DEPORTMENT. (Text, p. 169.) 1. *Identification.*—Observe the general appearance; color; odor; taste; and solubility in water and alcohol.

2. *Effect of Heat.*—Heat 1 gm. of citric acid slowly in a test tube. Is a "burnt sugar" odor detected?

3. *Reaction with Calcium Salts.*—Nearly neutralize 1 cc. of a 10 per cent water solution of citric acid with ammonium hydroxide. Then add 1 cc. of a 10 per cent calcium chloride solution. Result? Boil for 1 minute. Result? Compare with oxalic and tartaric acids.

4, 5, 6, 7. Perform tests Nos. 4, 5, 6 and 7 as under Tartaric Acid, p. 58. Results?

8. *Citric Acid in Fruit Juices.*—Devise an experiment to show the presence of citric acid in lemon juice. Perform the experiment after the method has been approved by an instructor.

9. *Summary.*—By arranging the preceding tests in tabular form show how oxalic, tartaric, and citric acids may be distinguished.

1-2

$2 NaNO_2 + H_2SO_4 \rightarrow Na_2SO_4 + 2HNO_2$

$HNO_2 + (C_2H_5 OH) \rightarrow C_2H_5-NO_2 + H_2O$

CHAPTER IX

ESTERS

62. Ethyl Nitrite. PREPARATION.—(Text, p. 175.) Connect a flask, dropping funnel, and receiving bottles as shown in Fig. 8. Pack the receiving bottles in ice or snow. Into the flask put 20 gm. of sodium nitrite dissolved in 80 cc. of water and 15 cc. of alcohol. After connecting the flask with the receiving bottles, add slowly through the dropping funnel in divided portions, 25 cc of water to which has just been added 8 cc. of concentrated sulphuric acid. The heat of the reaction will be sufficient to vaporize the ethyl nitrite formed, causing it to distil over into the bottles which act both as condensers and receivers. The acid must be added slowly, and the reagents must be well mixed. Avoid a too rapid reaction. Very low heat of a water bath may be used to drive over the last portions of ethyl nitrite.

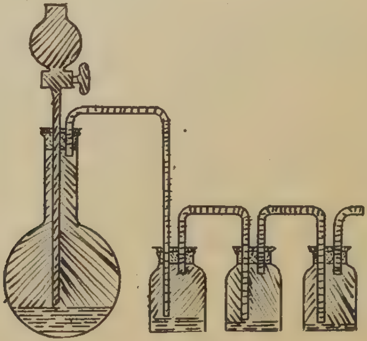


FIG. 8.

Wash the ethyl nitrite collected from the bottles with 10 cc. of ice water in a separatory funnel. Discard the washings. Then wash the ester with 10 cc. of ice water in which 1 gm. of sodium

Tetanal

Vebrifuge -

H_2O decomposes Ethyl nitrite

carbonate has been dissolved. Draw off the ethyl nitrite into a small glass-stoppered bottle. Add about 2 gm. of anhydrous poassium carbonate, stopper, shake well, and allow to stand for 15–30 minutes. Treat with a second portion of anhydrous potassium carbonate if necessary. When thoroughly dry, remove the potassium carbonate, put the ethyl nitrite in a vial and turn it in at the stock room.

1. Write equations to represent the main reactions involved in the preparation and purification of ethyl nitrite by the process described above.

Why is the very careful removal of water necessary in this case?

63. Isoamyl Nitrite. Preparation.—(Text, p. 176.) To 25 gm. of isoamyl alcohol in a small dry flask add 25 gm. of powdered sodium nitrite. Cool the mixture and maintain at a low temperature during the entire process. To the cooled mixture add gradually in divided portions, with shaking, 15 gm. of concentrated sulphuric acid. Equation. After all the acid has been added, shake the mixture at intervals during 15–20 minutes. Do not allow the temperature to rise.

3 [illegible] inhaled

angina pectoris

When the reaction has ceased, add carefully 70–80 cc. of water, or enough to dissolve the sodium sulphate that has been formed in the flask. Place the liquid in a separatory funnel and draw off and discard the sulphuric-acid-sodium-sulphate layer. *Do not discard the wrong portion.* Wash the amyl nitrite layer with water, draw off the amyl nitrite and dry it over anhydrous calcium chloride. Transfer the dried amyl nitrite to a small distilling flask, distil, using a water condenser and collecting and preserving that portion which distils at 96°–100°.

Heart disease with Pain

Caution.—Do not inhale the vapor of amyl nitrite, for a severe headache may be caused. Some persons are more susceptible than others.

(acetic Ether)

64. Ethyl Acetate. Preparation.—(Text, p. 180.) Pour into a dry distilling flask 30 cc. of ethyl alcohol and to it add carefully in divided portions, with shaking, 30 cc. of concentrated sulphuric acid. Do not allow the temperature to rise. Connect the side arm of the flask with a water condenser, and through the stopper of the flask insert a dropping funnel and a thermometer in

Ethyl Acetate

nitro Ethane - grap

amyl nitrite - fun

such a way that the ends of both are just under the surface of the liquid in the flask. Heat to 125° on a sand bath, and then add through the dropping funnel a mixture of 60 cc. of alcohol and 60 cc. of glacial acetic acid at such a rate that the temperature remains at or near 125°. Equation.

Heat for 10–15 minutes after the last portion of the acid-alcohol mixture has been added, stopping the distillation when a few cc. of the last portion of the distillate does not form two layers when mixed with an equal quantity of water.

Why does miscibility with water show that the distillation has been completed?

Place the impure ethyl acetate in a beaker and stir in sufficient 20 per cent solution of sodium carbonate to neutralize any acidity. Separate the two liquids by means of a separatory funnel, and shake the ethyl acetate layer with an equal quantity of saturated calcium chloride solution to remove any alcohol. Draw off the ethyl acetate and dry it over calcium chloride until the ester is clear and sparkling. It may be further purified by distillation, that portion which distils at 75°–79° being saved. Measure the amount of pure ethyl acetate obtained, and calculate its weight. Determine the percentage yield, basing the calculations on the amount of alcohol used.

DEPORTMENT. 1. *Physical Properties.*—Observe color; odor; density; volatility; and solubility in water and alcohol.

2. *Hydrolysis.*—To 10 cc. of ethyl acetate add 6 gm. of sodium hydroxide dissolved in 20 cc. of water. Boil under an air reflux condenser for 30–40 minutes, or until the odor of ethyl acetate is no longer perceptible. Equation.

Arrange for distillation with a horizontal water condenser, and distill off about 10 cc. Test the distillate for the presence of alcohol by the "iodoform" test. Result?

$CH_3COOC_2H_5 + NaOH \rightarrow$

$C_2H_5OH + CH_3COON$

Fat-digestive lipase [illegible]

sol in CCl_4 - [illegible] of the 4th

Saponification

$C_3H_5(O.OC\text{-}C_{15}H_{31})_3 + 3KOH \rightarrow C_3H_5(OH)_3 + 3C_{15}H_{31}\cdot C$

Palmitin K Palm

$C_3H_5(O.OC.C_{17}H_{35})_3 + 3KOH \rightarrow C_3H_5(OH)_3 + 3C_{17}H_{35}\cdot C$

Stearin K Stearate

CHAPTER X

FATS. OILS. SOAPS

65. Fats. Fixed Oils. DEPORTMENT. (Text, p. 181.) 1. *Solubilities.*—Test the solubility of separate small portions of lard, butter, and cottonseed oil in water, alcohol, chloroform, carbon tetrachloride, and benzin. Sol in benzine

2. *Effect of Cold.*—Cool 5 cc. of cottonseed oil to a low temperature, using a freezing mixture of ice and salt. Note the temperature at which coagulation takes place, and also the manner of congealing. Does the test indicate that this oil is a simple substance or a mixture of two or more substances? Explain. It Congeal [illegible]

3. *Effect of Heat.*—Put a few drops of cottonseed oil on a filter paper and warm gently. Does the oil volatilize? Is the stain permanent? Yes

4. *Presence of Unsaturated Compounds.*—Dissolve 3 gm. of butter and 3 gm. of cottonseed oil separately in 5 cc. portions of carbon tetrachloride. To each solution add drop by drop with shaking, a solution of bromine in carbon tetrachloride until the bromine is no longer decolorized. Which fat decolorizes the greater amount of bromine? Which fat contains the greater proportion of unsaturated compounds? What has become of the bromine which was used up? — new colorless compounds are formed

5. *Heat Production with Sulphuric Acid.*—Insert a thermometer in 10 cc. of cottonseed oil and record the temperature. To the oil add 5 cc. of concentrated sulphuric acid that is at the same temperature as the oil. Mix well with the thermometer. Note the temperature of the acid-oil mixture immediately after mixing. What change in temperature is noted? — MAUMENE TEST

The increase in temperature when sulphuric acid is added to fats and oils under specified conditions is the basis of the "Maumene Test" for the identity and purity of oils and fats.

Formation of glyceride

$C_3H_5(OH)_3 + 3HO.OC.C_{15}H_{31} \rightarrow C_3H_5(O.OC.C_{15}H_{31})_3 + 3$

(Palmitic acid) Glyceryl Tripalmitate

$_3H_5(OH)_3 + KHSO_4 \rightarrow CH_2{\cdot}CH{\cdot}CHO + KOH + H_2SO_4 + H_2O$

6. *Acrolein.*—To a few drops of oil or fat add 0.5 gm. of potassium hydrogen sulphate, and heat. Note the odor. acrolein odor

7. *Saponification.*—Saponify 5 gm. of butter with 5 cc. of a 50 per cent solution of sodium hydroxide, stirring and warming until a soap is formed. Put the soap mixture in a distilling flask, add 20 cc. of water, and sufficient dilute sulphuric acid to neutralize the excess of sodium hydroxide. Test with litmus. Distil, and collect about 5 cc. of distillate. Test its reaction to litmus.

Write an equation to represent the saponification of the glyceryl butyrate in butter. Write a second equation to show the action taking place when sulphuric acid is added.

In determining the "Reichert-Meissl Number" of butter, the procedure outlined above is followed, and the acid in the distillate is determined quantitatively.

8. *Ethyl Butyrate.*—Make the ethyl ester of the acid in the distillate in the preceding exercise, proceeding in the usual way. Outline the process used. Include an equation to represent the main reaction.

66. Soap. PREPARATION.—(Text, p. 186.) To 25 cc. of warm cottonseed oil in an evaporating dish or large beaker, add slowly with stirring 12 cc. of a 50 per cent warm solution of sodium hydroxide. Heat the emulsified oil over a very low flame until the mixture becomes homogenous. Stir frequently. If the mixture spatters badly, heat on a steam bath. Guard against boiling over. Keep the volume fairly constant by the addition of water.

After 30–45 minutes when the mixture appears to be homogeneous, remove a small portion and test for complete saponification. If the oil has been entirely saponified, the resulting soap should be entirely soluble in distilled water. If the soap does not dissolve completely on warming, the oil has not been entirely saponified, and the heating must be continued.

When complete saponification has been effected, pour the mass into a beaker, ointment pot, or cardboard box, and set aside until the next exercise.

and [illegible] 99% and

Assuming for this purpose that cottonseed oil is made up entirely of glyceryl oleate, write an equation to represent the reaction of saponification.

Deportment.—Using separate small pieces of the soap prepared as directed above, perform the following tests:

1. *Solubility.*—Test the solubility of soap in water, alcohol, ether, and benzin.

2. *Alkalinity.*—To a concentrated soap solution made with distilled water, add a few drops of phenolphthalein solution. Result? Perform the same test upon a concentrated alcoholic solution of the soap. Result? Compare the results of these tests with those performed upon commercial soaps later in this exercise.

Dissolve about 10 gm. of the soap you have made in 100 cc. of distilled water. Divide the solution into three parts. Use the separate portions for the following tests:

3. *Reaction with Sodium Chloride.*—To a portion of the soap solution add an equal volume of a saturated solution of sodium chloride. Result?

Explain in terms of ions the reaction that has taken place.

Filter off the precipitated soap, and test the filtrate for glycerin as follows:

4. *Glycerin.*—Evaporate the filtrate from the preceding exercise nearly to dryness. Dissolve the residue in 10 cc. of alcohol, filter, and allow the alcohol to evaporate spontaneously. The residue left is an impure glycerin. Identify it by the borax bead test (p. 46). To a portion of the glycerin residue add a little finely powdered potassium hydrogen sulphate and heat strongly. An odor of acrolein shows the presence of glycerin.

Should you expect to find glycerin in ordinary hard soap? Why should it be present in the soap you made?

5. *Action with Calcium Salts.*—To the second portion of aqueous soap solution previously prepared add 5 cc. of a concentrated aqueous solution of calcium chloride. Result? Equation.

Why do laundries prefer to use "soft" water? Why is a calcium soap valueless for cleansing? Explain the difference in action of sodium chloride and calcium chloride on soap solution.

6. *Action with Acids.*—Acidulate the third portion of soap solution with hydrochloric acid. Equation. Test the solubility of the precipitate in water, alcohol, ether, and sodium hydroxide solution.

By considering solubilites alone, how could one distinguish between a fat, a fatty acid, and a soap?

67. Commercial Soaps. 1. *Alkalinity.*—Place a few drops of phenolphthalein solution on small pieces of ivory soap and yellow laundry soap. Results?

Why do certain people test the quality of Castile soap by its taste?

2. *Hydrolysis.*—To a *very concentrated* water solution of ivory soap add phenolphthalein solution. Result? Dilute the solution largely with distilled water. Result? Explain.

3. *Unsaponified Fat.*—Shake 5 gm. of powdered soap with 15 cc. of petroleum ether in a stoppered flask for several minutes. Filter. Allow the filtrate to evaporate spontaneously. (Care!) Any residue left is unsaponified fat.

Should you expect to find unsaponified fat and free alkali in the same soap? Explain.

4. *Transparent Soaps.*—Heat 10 gm. of powdered soap with 50 cc. of alcohol on a water bath under a reflux condenser until the soap has nearly or entirely dissolved. Filter while hot. (Care!) Set the filtrate aside in a warm place to evaporate spontaneously. Observe the residue which remains. What physical change has taken place in the soap?

Fat - insol in H_2O Sol in CCl_4
Soap - sol " " sol in C_2H_5-OH
Fat sol in petroleum ether
Soap - insol " " "

2-6-31

CHAPTER XI

CARBOHYDRATES

68. Detection. (Text, p. 197.) *Molisch Test.*—This test should react positively with all carbohydrates.

Make dilute water solutions of glucose, sucrose, lactose, and any other soluble carbohydrates. To 2 cc. of each solution add 2 drops of 10 per cent solution of alpha naphthol in chloroform (Molisch's reagent). Then carefully pour down the side of the inclined test tube 4 cc. of chemically pure concentrated sulphuric acid in such a way that the liquids do not mix, but form two layers. A reddish-violet zone at the point of contact shows the presence of a carbohydrate.

MONOSACCHAROSES

69. Glucose. Deportment.—(Text, p. 200.) Use crystallized dextrose or glucose, U.S.P., for the following tests:

1. *Sweetness.*—Note the relative sweetness of glucose as compared with sucrose.

2. *Solubility.*—Determine the solubility of glucose in water, alcohol, and chloroform. very sol. in H_2O sparingly sol. in alc.

3. *Action with Sulphuric Acid.*—Pour a few drops of cold concentrated sulphuric acid on some crystalline dextrose. Result? - a brown sugar is present.

✓ Use a 1 per cent solution of glucose for the following tests.

4. *Reducing Action.*—Determine if the glucose solution will reduce Fehling's solution. - yes

✓ 5. *Benedict's Test.*—To 5 cc. of Benedict's qualitative reagent add a few drops of the glucose solution and heat. Boil for 1–2 minutes. A $\overset{\text{least}}{\text{greenish}}$, yellow, or $\overset{\text{most}}{\text{red}}$ precipitate should appear.

✓ 6. *Böttinger's Test.*—To 5 cc. of glucose solution add 5 cc. of a 50 per cent solution of sodium hydroxide and about 0.2 gm. of bismuth subnitrate. Boil for 5 minutes. A grayish to black precipitate of metallic bismuth should be produced.

Reducing action of sugar

$2KOH + 2BiONO_3 \rightarrow 2KNO_3 + Bi_2O_3 + H_2O$

7. *Moore's Test.*—Heat 5 cc. of glucose solution with 5 cc. of sodium hydroxide T.S. Compare the appearance of the solution after heating, with a portion of the same mixture that has not been heated. Result? Compare with the action of caustic alkalies on aldehydes.

Fehling's, Benedict's, Moore's and Böttinger's tests are used to detect "sugar" in the urine.

8. *Glucosazone.*—To 0.3 gm. of glucose dissolved in 4 cc. of water add 0.6 gm. of colorless phenylhydrazine hydrochloride and 0.6 gm. of sodium acetate. Place the test tube containing the mixture in a beaker of boiling water for 15 minutes or until a good precipitate is obtained. Note the time taken for the production of the precipitate. Cool the liquid, and examine the crystals under a microscope. Sketch their appearance. The melting points of the osazones of the various carbohydrates, as well as their microscopic appearance, are characteristic enough to serve as a means of identification of the carbohydrate.

In using this test on other carbohydrates, the same procedure is followed. The mixture need never be heated for more than 30 minutes. In some cases precipitation occurs only on cooling.

DISACCHAROSES

70. Sucrose. DEPORTMENT.—(Text, p. 206.) (1–8) Using pure sucrose perform tests Nos. 1 to 8 inclusive as described under Glucose. Saccharum ustum, Burnt sugar coloring

N.F.

✓ 9. *Caramel.*—Heat carefully 3–4 gm. of sucrose in a dry test tube until the sucrose melts and turns brown. Cool. Test the solubility of the brown substance in water. Note its taste.

10. *Inversion.*—Make 20 cc. of a 1 per cent solution of sucrose. Test a portion to determine if it reduces Fehling's solution. Result? To the remainder of the solution add 1 cc. of diluted hydrochloric acid and boil for 10 minutes. Neutralize with sodium hydroxide T.S., and test a small portion to determine its action on Fehling's solution. Result? What effect did heating with acid have upon the sucrose?

Why was the sugar solution neutralized with sodium hydroxide T.S. before testing with Fehling's solution?

Fehling's only acts in an alkaline media
– alkaline copper tartrate T.S.!

H_2SO_4 + lactose = a [illegible] –
sugar is present

71. Lactose. Deportment.—(Text, p. 211.) (1–8) Using pure lactose, perform tests Nos. 1–8 inclusive as described under Glucose, and record the results.

72. Optical Activity. Demonstration.—(Text, p. 161. United States Pharmacopoeia, X, pp. 447–449.) Dissolve exactly 52 gm. of sucrose in enough warm distilled water to make 200 cc. Mix well. Allow to cool to 20°, and make up exactly to 200 cc. with distilled water. Mix well. Fill a one-decimeter tube with the solution, place in a polarimeter, and determine the direction and angle of rotation.

Fill a two-decimeter tube with the same solution, and determine the angle of rotation. How does it compare with that observed in the one-decimeter tube?

From the information gained, calculate the specific rotation of sucrose.

By "specific rotation" is meant the rotation, expressed in degrees, caused by a solution containing 100 gm. of the substance dissolved in 100 cc. of the solution when a tube 1 decimeter long is used. With most substances it is not possible to determine the specific rotation for a 100 per cent solution. It can be calculated from the observed rotation of solutions whose strength is known.

The symbol, $(a)_D$, is used to indicate specific rotation with the sodium flame. Use the following formula in calculating the specific rotation of the sucrose solution:

$$(a)_D = \frac{a \times 100}{1 \times c}$$

a, is the observed rotation; c, the concentration, that is the number of grams in 100 cc. of solution; 1, is the length of the tube in decimeters.

UNCRYSTALLIZABLE POLYSACCHAROSES

73. Starch. Deportment. (Text, p. 212.) 1. *Appearance.* Examine corn and potato starches under the microscope and make a drawing to show the relative size and the characteristic appearance of each.

2. *Molisch Test.*—Perform the Molisch test on about 0.1 gm. of starch. Allow the mixture to stand for some time. Result?

3. *Starch Paste.*—Stir 5 gm. of starch in 35 cc. of cold water and heat the mixture up to boiling while stirring vigorously.

Cool, and use separate portions of the paste for the following tests.

4. *Iodine Test.*—Add a drop of very dilute solution of iodine to a portion of the starch paste. Result? Heat to boiling. Result? Allow to cool. Result?

5. *Reducing Action.*—Test the action of starch paste on Fehling's solution. Result?

6. *Action of Saliva.*—Place a test tube containing a mixture of 5 cc. of starch paste and 5 cc. of saliva in a beaker of water warmed to 40°. Note any changes in consistence or opalescence during 15 minutes' standing. At two minute intervals from the beginning of the heating remove a drop or two of the mixture on a glass rod and test it on porcelain with a drop of iodine T.S. Note the time required to invert the starch completely. Complete inversion of the starch will have taken place when there is no blue color produced on adding the iodine. Observe the production of intermediate colors as the test proceeds. To what are the intermediate colors due?

7. *Reducing Action of Inverted Starch.*—When the iodine test in the preceding exercise shows complete inversion of the starch, test a portion of the mixture with Fehling's solution. Result? Test some saliva with Fehling's solution. Result? Why is the latter test necessary to verify the result of the Fehling test on inverted starch?

8. *Taste.*—Hold some starch paste in the mouth for some time. Taste at first? Taste later? Explain the change. Perform the same test with a portion of dry starch. Result?

9. *Acid Hydrolysis.*—Boil 15 cc. of starch paste with 10 cc. of water and 1 cc. of concentrated hydrochloric acid. At three minute intervals remove a drop of the starch solution and test with iodine T.S. Note the time for the complete inversion of the starch. After inversion, neutralize the solution with sodium hydroxide and test a portion of it with Fehling's solution. Result?

/ **74. Dextrin.** PREPARATION.—(Text, p. 214.) Heat 5–10 gm. of dry starch in an evaporating dish on a sand bath at about 220° for 20–25 minutes. Stir with a glass rod. Be careful to avoid scorching of the starch by overheating. As the heat is applied, a yellowish or brownish color will develop. At the end

erythrodextrin [illegible] malto-dextrin – [illegible]
[illegible]

of the heating add 2–3 cc. of water and stir. Note the adhesive quality. Then add 35 cc. of water, stirring well to dissolve as much of the solid matter as possible. Filter off the unconverted starch, and use the filtrate in the following tests.

Deportment. 1. *Reducing Action.*—Test a portion of the liquid with Fehling's solution. Result? – [illegible]

2. *Iodine Test.*—Test a portion of the liquid with a little iodine T.S. Result? – Wine-red

3. *Action with Alcohol.*—To 3 cc. of the solution add 10 cc. of alcohol. Result? Filter off and dry the precipitate. What is the precipitated material? Perform the iodine test upon it. Result? [illegible]

5% [illegible]

4. *Dextrin in Bread.*—Test a piece of toasted bread for the presence of dextrin by making a concentrated water solution of the toast, filtering, and testing the filtrate with iodine T.S. Result? Perform the same test upon a water solution of untoasted bread from which the crust has been removed. Result? Perform the same test on the bread crust. Result?

75. Cellulose. (Text, p. 215.) 1. *Reducing Action.*—Test some small pieces of washed filter paper with Fehling's solution. Result?

2. *Iodine Test.*—Test some pure filter paper with iodine T.S. Result? – not colored (547) [illegible]

3. *Solubility.*—Test the solubility of cellulose (cotton) in Schweitzer's reagent. Result? Add a large excess of water. Result?

4. *Acid Hydrolysis.*—To a piece of filter paper about 4 cm. square add 1 cc. of concentrated sulphuric acid and rub well in a mortar. Dilute carefully with 50 cc. of water, and boil for 30 minutes. Neutralize the solution with sodium hydroxide T.S. and test with Fehling's solution. Result?

5. *Parchment Paper.*—Immerse some strips of filter paper in cold 60 per cent sulphuric acid for 15–20 *seconds*. Remove, and wash immediately with running water. Rinse in very dilute ammonium hydroxide and again wash in running water. Dry. Compare the toughness of the treated paper while wet with a piece of wet filter paper. Compare the strength of the dry parchment paper with that of a piece of dry filter paper. Test

[illegible] – Schweitzer's

the parchment paper, both while wet and after drying, with a drop of iodine T.S. Results?

6. *Cellulose Nitrates.*—Place 0.5 gm. of cotton in a mixture of 10 cc. of concentrated nitric acid and 15 cc. of concentrated sulphuric acid immediately after the acids have been cautiously mixed. Stir the cotton about with a glass rod for not over 5 minutes. Then withdraw the nitrated cotton with the rod, press out as much of the acid liquid as possible by means of the rod, and wash the mass thoroughly in running water. Allow it to dry at room temperature.

Observe the appearance and note the feeling of the dry nitrated cotton. Compare with untreated cotton. Test the solubility of the dry cellulose nitrate in alcohol, chloroform, ether, and in a mixture of 1 part of alcohol and 3 parts of ether. (Care!)

Dissolve the remainder of the nitrated cellulose in the alcohol-ether mixture, decanting the solution from any undissolved residue. Such a solution of cellulose nitrate is called "collodion." Allow a few cc. of the collodion to stand exposed to the air in an evaporating dish so that the solvent may evaporate. Result ? Place a few drops of the collodion on the skin. Result?

76. Lignin.—(Text, p. 215.) To 1 cc. of aniline add 1 cc. of hydrochloric acid, followed by 5 cc. of water. Moisten a piece of newspaper with a portion of the solution, and pieces of linen writing paper and other kinds of paper with the remainder. Note the presence of lignin in the newspaper and other cheap grades of paper as evidenced by the production of a characteristic color.

$C_{18}H_{30}O_{15}$ – Lignin

2-13-31

CHAPTER XII

ACTION OF ENZYMES

77. Digestion.—(Text, p. 230.) In each of 6 test tubes put about 2 gm. of finely ground hard-boiled white of egg. In 2 other tubes place the same amount of egg-white in a single piece. Label the tubes A to H.

To tube A, add 10 cc. of water.
To tube B, add 10 cc. of water and 0.1 gm. of pepsin.
To tube C, add 5 cc. of water and 5 cc. of N/10 hydrochloric acid.
To tube D, add 5 cc. of water, 5 cc. of N/10 hydrochloric acid and 0.1 gm. of pepsin.
To tube E, add 5 cc. of water, 5 cc. of N/10 hydrochloric acid, and 0.1 gm. of pancreatin.
To tube F, add 10 cc. of water, 1 cc. of N/10 sodium hydroxide, and 0.1 gm. of pancreatin.
To tube G, containing a single piece of egg-white, add the same reagents as in tube D.
To tube H, containing a single piece of egg-white, add the same reagents as in tube F.

After preparing and labeling the tubes, shake well, and place the tubes in a beaker of water and keep at about 40° for 3 hours. Examine the tubes at intervals of one-half hour. In which tubes has digestion taken place most completely and most rapidly? What conditions are necessary for stomach digestion? For intestinal digestion? Has evidence been obtained to prove that thorough mastication of the food is to be desired? Yes

78. Effect of Heating Milk.—To 10 cc. of raw milk add 2 drops of peroxide of hydrogen solution, 3 per cent, and 4 drops of a freshly prepared 2 per cent solution of paraphenylenediamine. Shake. Note the dark violet color which is produced at once.

Perform the same test on 10 cc. of milk which has been *boiled* and cooled. Result?

Heat 10 cc. of milk to exactly 75°, using a thermometer and stirring while the milk is being heated. Cool, and apply the paraphenylenediamine test. Result?

Heat 10 cc. of milk to exactly 82° in the same way. Cool, and perform the paraphenylenediamine test. Result?

The color produced in the preceding tests is probably due to the action of enzymes which are injured by heating. Is it possible to detect by this test milk which has been pasteurized at the usual temperature?

Extraction of caffeine from tea.

2-13-31

Know chemical formula

$(CH_2)_6N_4$

CHAPTER XIII

NITROGEN COMPOUNDS

79. Methenamine. Preparation.—(Text, p. 243.) To 25 cc. of solution of formaldehyde in an evaporating dish under a hood, *add slowly, with constant stirring*, 15 cc. of stronger ammonia water. If the liquid does not have a distinct odor of ammonia, more ammonium hydroxide should be added. Equation.

Slowly evaporate the mixture over a low flame until its volume has been reduced nearly one-half. Filter if necessary. Continue the evaporation until only about one-fourth of the original volume is left. Set the liquid aside to cool, and crystallization will take place. Filter off the crystals and wash them on the filter paper with alcohol until the washings are clear. Dry at room temperature. Recrystallization from hot water may be necessary in order to obtain colorless crystals if pure ammonium hydroxide and pure formaldehyde have not been used.

Deportment. 1. *Heat.*—Place about 2 gm. of methenamine crystals in a crucible and ignite. Note the large amount of heat given off.

2. *Reaction with Sulphuric Acid.*—Heat an aqueous solution of methenamine with dilute sulphuric acid. Formaldehyde is liberated; ammonium sulphate remains in solution.

80. Urea. Preparation.—(Text, p. 251.) To 10 gm. of potassium cyanate dissolved in a small amount of water in an evaporating dish, add 10 cc. of saturated ammonium sulphate solution. Equation. Evaporate to *dryness* on a water bath. Equation. Stir frequently so that a crust will not form and hinder the escape of steam. Transfer the dry residue to an Erlenmeyer flask, add 20 cc. of alcohol, and heat just to boiling on a water bath guarding against the ignition of the alcohol vapor. Filter the alcoholic solution into an evaporating dish and allow the alcohol to evaporate spontaneously. Crystals of urea will be formed.

DEPORTMENT. 1. *Urea Nitrate.*—To a small amount of urea dissolved in a few drops of water add a drop or two of concentrated nitric acid. Crystals of urea nitrate will be formed. Equation.

2. *Reaction with Nitrous Acid.*—To 0.3 gm. of urea dissolved in 2 cc. of water, add 1 cc. of 10 per cent solution of sodium nitrite, followed by 0.5 cc. of concentrated hydrochloric acid. Note the effervescence. Nitrogen and carbon dioxide are given off. Equation.

3. *Reaction with Alkalies.*—Dissolve 0.5 gm. of urea in 2 cc. of water and add 2 cc. of sodium hydroxide T. S. Odor? Reaction of the vapor to wet litmus paper? Equation.

4. *Reaction with Hypobromites.*—To a dilute solution of urea add 1 cc. of an alkaline solution of sodium hypobromite. Nitrogen and carbon dioxide are given off. Equation.

A process for the determination of the amount of urea in the urine based on this reaction was in use for many years.

5. *Biuret Reaction.*—Heat 0.5 gm. of urea in a test tube at first gently and then more strongly until an opaque white solid containing biuret, $HN(OCNH_2)_2$, is obtained. Observe the odor and reaction of the vapor. Cool, shake with 2 cc. of sodium hydroxide T.S., and then add a drop or two of a dilute solution of cupric sulphate. A reddish to violet color is produced.

This test is not characteristic of urea alone, but responds when applied to any compound having at least two HN-CO groups. It is useful in the detection of certain proteins.

82. Caffeine. PREPARATION.—(Text, p. 258.) Boil 5–10 gm. of coffee or tea in 250 cc. of water for 15 minutes. Strain or filter. Remove the tannin and extractive matter from the filtrate by adding a solution of lead subacetate drop by drop as long as a precipitate is formed. Filter. If an excess of lead subacetate has been used, it must be removed by adding sulphuric acid to the filtrate as long as a precipitate is produced. Filter if necessary.

Concentrate the clear solution to about 40 cc. Filter if there is a precipitate and extract the cold solution in a separatory funnel with 20 cc. of chloroform. Filter the chloroform solution into a beaker, cover with a filter paper to keep out dust, and allow the chloroform to evaporate. The residue of caffeine can be purified by sublimation.

Optional Method.—Macerate 5 gm. of powdered guarana in a flask with 100 cc. of chloroform and 5 cc. of ammonium hydroxide. Stopper well and shake occasionally. Let stand for four hours or more. Filter off the chloroform, which contains the caffeine, and evaporate to dryness at room temperature or with very low heat. Dissolve the residue in dilute sulphuric acid, heating gently. Filter into a separatory funnel, add ammonium hydroxide to alkalinity, and shake with three separate portions of chloroform of 10 cc. each. Evaporate the combined chloroform solutions at low heat. The residue is caffeine.

DEPORTMENT. 1. *Solubility.*—Determine the solubility of caffeine in water, alcohol, and ether. Its solubility in chloroform has been demonstrated by the method of extraction.

2. *Identification.*—Dissolve 0.01 gm. of caffeine in 1 cc. of hydrochloric acid in a porcelain dish. Add 0.1 gm. of potassium chlorate and evaporate to dryness on a water bath. A reddish-yellow to pink color will be obtained. Invert the dish containing the residue over a beaker containing a few drops of ammonium hydroxide. The residue becomes puplish in color. The purple color is destroyed by adding a few drops of sodium hydroxide T.S.

3. *Reaction with Tannic Acid.*—To a saturated aqueous solution of caffeine add a solution of tannic acid until there is an excess of the reagent. Result at first? Result later?

4. *Reaction with Iodine.*—To an aqueous solution of caffeine add a few drops of a water solution of iodine. Result? Perform the same test on an aqueous solution of caffeine after acidulating with hydrochloric or sulphuric acid. Result? opt

5. *Reaction with Mayer's Reagent.*—To an aqueous solution of caffeine add a few drops of mercuric-potassium iodide T.S. (Mayer's reagent.) Result?

6. *Investigation.*—Perform suitable tests to demonstrate the presence or absence of caffeine in coca cola or similar soda-fountain beverage. Report the method, and the result of the investigation.

Present

CHAPTER XIV

CLOSED-CHAIN HYDROCARBONS. VARIOUS DERIVATIVES

HYDROCARBONS

82. Benzene. PREPARATION. (Text, p. 301, Man., p. 7.) **Caution.**—Flames!

Dissolve 6 gm. of sodium hydroxide in 15 cc. of hot water and slowly stir in 5 gm. of benzoic acid. Heat to dryness in an evaporating dish, stirring, and being careful not to carbonize the mass by overheating. Powder the intimately mixed sodium hydroxide and sodium benzoate and put it in a strong test tube that has been carefully fitted with a rubber stopper and an exit tube 50 cm. long leading into another test tube in which the distillate is to be collected. Heat the mixture slowly at first and then with increased heat, keeping the distillate cold by placing the receiving tube in a beaker of ice water. Equation.

Heat as long as any distillate is obtained. Dry the distillate by shaking it with small pieces of calcium chloride.

Guard against the ignition of the benzene vapor. If the glass tube cracks on heating, extinguish the flame immediately. Cool the mixture and transfer it to another tube. Do not disconnect the apparatus at the end of the operation until the apparatus is cold.

1. *Test of Residue.*—Add dilute hydrochloric acid to a portion of the solid matter left in the generating tube. Result? Equation.

DEPORTMENT.—Use pure benzene for the following tests:

2. *Identification.*—Observe general appearance; mobility; volatility; odor; density; inflammability; solubility. In each respect, compare with petroleum benzin.

3. *Melting Point.*—Set a test tube containing 10 cc. of benzene in a freezing mixture of ice and salt. Stir the benzene constantly with a thermometer, and by alternately removing and inserting the tube in the freezing mixture cause a gradual reduction in the

temperature of the benzene. Observe the temperature at which the liquid and crystals are in equilibrium, and report it as the melting point of benzene.

4. *Reaction with Sulphuric Acid.*—Shake 2 cc. of benzene with 4 cc. of concentrated sulphuric acid. Result? Is the benzene dissolved? Is there discoloration of either liquid? Compare with benzin.

5. *Saturation.*—Shake 5 cc. of benzene with 3 cc. of dilute alkaline potassium permanganate solution. Does benzene act like a saturated or an unsaturated compound? After standing a few minutes, warm the mixture gently. Is the presence of a multiple bond indicated?

6. *Reaction with Bromine.*—To 5 cc. of benzene add 3 cc. of bromine water, and shake. A drop or two of bromine may be used instead of bromine water. Add a small tack or a few iron card teeth to act as a contact agent. Is the bromine color destroyed? Why? Equation. Breathe across the mouth of the tube. What causes the mist observed?

7. *Reaction with Nitric Acid.*—Mix 2 cc. of concentrated nitric acid with 2 cc. of concentrated sulphuric acid. To the mixture under the hood, add with shaking, a few drops at a time, 2 cc. of benzene. The reaction may be vigorous. Hold the mouth of the tube away from you. Allow the mixture to stand for a few minutes and then pour it into an excess of cold water. The oily-appearing liquid which separates is nitrobenzene. Equation. Observe the odor of nitrobenzene, but do not inhale the vapor freely. Do not allow nitrobenzene to come in contact with the skin.

83. Oxidation of a Side Chain.—To 5 cc. of toluene contained in a small round-bottomed flask add 3 gm. of powdered potassium permanganate and 40 cc. of water to which 10 cc. of sulphuric acid has been added. (Care!) Attach a reflux condenser and heat for 1.5–2 hours, shaking at frequent intervals to insure thorough contact of the toluene with the oxidizing mixture. Equation.

Cool, and extract the reaction mixture with 15 cc. of ether. Allow the ether to evaporate spontaneously. What is the compound left? Identify it by chemical tests. Record the tests used.

HALOGENATION

84. Monobrombenzene. PREPARATION.—(Text, p. 311. Man., p. 7.) Have the apparatus set-up approved by an instructor before beginning the exercise.

In a 300 cc. Erlenmeyer flask under a hood mix 25 cc. of benzene with 15 cc. of bromine. (Care!) Cool the flask by placing it in a larger container which holds ice or ice water. Stopper the flask with a tightly-fitting stopper through which passes a glass tube bent twice at right angles to form a letter U, one arm of which is longer than the other. The longer arm should be about 75 cm. long, and should pass just through the cork stopper of the flask. To the shorter end connect a small glass funnel. Arrange the apparatus so that the funnel reaches nearly to, but *does not touch* the surface of 200 cc. of water, or better, a solution of sodium hydroxide held in a beaker. This arrangement serves to absorb the hydrogen bromide which is given off. If the apparatus is well set up, this exercise can be performed in the open laboratory without inconvenience. Bromine, however, should be measured and transferred from one container to another under a hood.

To the cold mixture of bromine and benzene add a couple of tacks or a few card teeth, connect up the apparatus and allow the reaction to proceed to completion. Equation. If the reaction is slow in starting, remove the flask from the ice water for a few minutes. If necessary, use a bath of warm water to start the reaction. Check the speed of the reaction by the use of the ice-water bath, being careful not to permit the reaction to become vigorous enough to carry over bromine vapor. The greater part of the reaction will have been completed within 1.5–2 hours. The reaction mixture may be permitted to stand over night.

When the reaction is complete, dry the outside of the reaction flask, unstopper it and heat it under a hood with a small, constantly moving flame until bromine vapor is no longer given off. Wash the oily liquid remaining several times with water in a separatory funnel. The last washing should contain a little sodium hydroxide T.S. to combine with any bromine or hydrobromic acid that may remain. Dry over anhydrous calcium chloride. Purify by redistillation using an air condenser and reserving that portion of the distillate that comes over at 145°–160°. Save the residue in the distilling flask.

DEPORTMENT. 1. *Properties.*—Note the appearance; odor; density; volatility; solubility; and inflammability.

2. *Halogen Tests.*—Test a portion of monobrombenzene with nitric acid and silver nitrate T.S. to detect the presence of halogen ions. Result? Perform the copper wire test for halogens. Result?

85. *p*-Dibrombenzene. PREPARATION.—When the material in the distilling flask used in the preceding exercise cools, crystals of *p*-dibrombenzene may be deposited. Filter, dissolve the crystals in hot alcohol, filter again and allow the alcohol to evaporate spontaneously.

SULPHONATION

86. Benzenesulphonic Acid and Sodium Benzenesulphonate. PREPARATION.—(Text, p. 312.) In a flask fitted with a reflux condenser put 35 gm. of fuming sulphuric acid. (Sp. Gr. 1.89.) Through the condenser add 10 gm. of benzene, 0.5 cc. at a time, with constant vigorous shaking so that each portion of the benzene as it is added is taken up by the benzene and does not form a separate layer. Heat gently on a water bath for about 1 hour, when the reaction will be complete. The mixture now contains benzenesulphonic acid and an excess of sulphuric acid. Equation.

The benzenesulphonic acid is most easily separated from the excess of sulphuric acid in the form of its sodium salt, sodium benzenesulphonate, which is insoluble in a saturated solution of sodium chloride. Slowly pour the reaction mixture with stirring into 150 cc. of warm saturated solution of sodium chloride. Stir, filter, rejecting the precipitate of diphenylsulphone, $(C_6H_5)_2SO_2$, which forms. Cool the filtrate rapidly by using an ice pack, and the sodium benzenesulphonate will separate out in flaky crystals. Allow the mixture to stand for an hour, filter, and wash the crystals on the filter with a fresh portion of salt solution. Dry on filter paper at room temperature. Recrystallize from dehydrated alcohol if it is necessary to remove the small amount of sodium chloride which remains.

Turn in the purified crystals at the stock room.

NITRATION

87. Nitrobenzene. PREPARATION. (Text, p. 314). **Caution.**—Do not allow nitrobenzene to touch the skin. Do not inhale its vapor freely. In this exercise, temperature conditions must be controlled exactly.

To 30 gm. of concentrated sulphuric acid in an Erlenmeyer or round-bottomed flask carefully add 20 gm. of concentrated nitric acid. Mix, and cool the mixture by flowing tap water over the flask. Attach a reflux condenser, and through it add to the mixture of acids 15 gm. of benzene, in 2 cc. portions, 3 minutes apart, with *constant shaking*. The temperature, which will rise as the benzene is added, must be kept at about 50° by flowing cold water over the flask as necessary. The thermometer should extend *into* the reaction mixture. Equation.

Place the flask and attached condenser in a water bath and keep the water at 50°–60° for a half-hour or more. The flask should be shaken rather vigorously every 5 minutes to insure thorough mixing of the reacting materials.

Too high a temperature at this point will cause a decreased yield of nitrobenezene by increasing the amount of dinitrobenzene. Too low a temperature will also give a smaller yield by leaving some of the benzene unaffected.

When the reaction is complete, cool, and pour the mixture into a separatory funnel, separate and discard the acid mixture. Wash the nitrobenzene in the separator with water two or three times, and *neutralize it carefully* with sodium hydroxide T.S. Wash with water again, and dry over calcium chloride. After testing again to make sure that no free acid is present, distil, using an air condenser and changing the receiver and reserving that part of the distillate which comes over at 200°–208°. *Do not heat beyond* 208°.

The residue left in the distilling flask is mainly *m*-dinitrobenzene. It may decompose violently if heated at too high a temperature. It is for this reason that the distillation is stopped at 208°. The dinitrobenzene can be obtained by crystallization from alcohol.

Why is the benzene added to the nitrating mixture rather than the nitrating mixture to the benzene?

CHAPTER XV

AMINES AND THEIR DERIVATIVES

88. Aniline. PREPARATION. (Text, p. 316. Man., p. 14.) **Caution.**—Do not inhale the vapor of aniline. Do not allow aniline to touch the skin. In this exercise hydrogen is generated. Take all necessary precautions to prevent accidents.

In a large flask place 20 gm. of tin and 10 gm. of nitrobenzene. Connect the flask with a reflux condenser and add through the condenser 45 gm. of concentrated hydrochloric acid in 5 cc. portions, several minutes apart, shaking well after each addition. Warm gently if necessary to start the reaction, and cool by immersing the flask in cold water if the reaction becomes too rapid. Do not hurry. Avoid a vigorous boiling. Keep the reaction going gently and steadily but do not let it become so rapid that vapors escape from the condenser.

When the reaction slows down after the last portion of the acid has been added, heat the flask on a water bath for one-half hour, shaking occasionally. Equation. Guard against a sudden violent reaction when the flask is heated. This may occur if the temperature has been kept so low that considerable nitrobenzene has not been reduced.

At the end of the heating no oily drops of nitrobenzene should be seen in the flask. To the warm reaction mixture add slowly a 50 per cent solution of sodium hydroxide until the reaction of the well-shaken mixture is strongly alkaline. Cool by flowing cold water over the flask if the addition of the alkali causes the mixture to boil. Then distil with steam until the distillate comes over clear.

Saturate the distillate with sodium chloride, place the solution in a separatory funnel, and extract the aniline with two portions of 10 cc. each of ether. Dry the combined ether solutions over small pieces of solid sodium hydroxide. Filter the dried solution into a dry beaker, cover with filter paper, and allow the ether to evaporate spontaneously, away from flames. The residue is an impure aniline. It may be purified by redistillation from a small flask or test tube.

DEPORTMENT. 1. *Identification.*—Observe general appearance; odor; density; inflammability; and test solubility in water, dilute hydrochloric acid, chloroform, and benzene.

2. *Aniline Sulphate.*—To 10 cc. of water add 5 cc. of aniline and 3 cc. of concentrated sulphuric acid. Boil. Set the mixture aside to crystallize. Equation.

To a water solution of aniline sulphate add an excess of sodium hydroxide T.S. Result? Equation.

3. *Tribromaniline.*—To 3 cc. of a water solution of aniline add bromine water drop by drop until a yellowish color persists after shaking. Tribromaniline is formed. Equation.

4. *Identification Tests.*—(a) To 3 cc. of a water solution of aniline add 0.5 cc. of a dilute solution of ferric chloride. Result?

(b) To 3 cc. of a water solution of aniline add 5 cc. of a saturated aqueous solution of chlorinated lime or of sodium hypochlorite. Result?

(c) To a few drops of aniline in an evaporating dish add a crystal of potassium dichromate and a drop or two of concentrated sulphuric acid. Note any color changes. Heat the dish on a water bath. Result?

5. *Carbylamine Reaction.* **Hood.**—In a test tube under a hood warm a drop of aniline and a drop of chloroform with 1 cc. of an alcoholic solution of potassium hydroxide. Observe the odor cautiously. Equation. Dispose of the mixture at once as directed.

83. p-Sulphanilic Acid. PREPARATION.—(Text. p. 317.) To 30 gm. of concentrated sulphuric acid in a round-bottomed flask add gradually 15 gm. of freshly distilled aniline, with careful and constant shaking. Heat on an oil bath to 180°–190° for 4 to 5 hours, or until the reaction is complete. Equation. The reaction is finished when a few drops of the reaction mixture will mix with sodium hydroxide T.S. without separation of oily drops of aniline.

SAPONIFICATION

At the end of the heating pour the mixture into 300–400 cc. of cold water. Filter, reject the filtrate, and wash the crystals on the filter paper with cold water. Recrystallize from boiling water. Use charcoal to decolorize if necessary. Dry the crystals at room temperature. Weigh, and calculate the percentage yield, basing the calculation on the amount of aniline used.

90. Acetanilid. PREPARATION.—(Text, p. 318.) Mix 20 cc. of freshly distilled aniline with 25 cc. of glacial acetic acid in a 300 cc. flask. Connect with a reflux condenser and boil *very gently* for 6–7 hours, or until a small portion of the mixture solidifies when dropped into cold water. Equation.

If desired, an air condenser about 1.5 meters long can be used instead of a water condenser.

EQUATION - FORMULA - GRAPH

At the end of the heating, pour the warm mixture into about 500 cc. of cold water, filter through a fluted paper, and allow the filtrate to cool. Crystals of acetanilid will be deposited. Recrystallize from hot water, using charcoal if necessary to obtain colorless crystals. Dry at room temperature. Determine the melting point of your product, and compare it with the melting point of pure acetanilid. Calculate the percentage yield, basing the calculation on the amount of aniline used.

91. Identification of Acetanilid, Acetphenetidin, and **Antipyrine.**—(United States Pharmacopoeia, X, pp. 9, 11, 51.) Obtain an "unknown" sample at the stock room and identify it as acetanilid, antipyrine, or acetphenetidin. The following tests will be helpful: 3-1

Acetanilid.—Melting point, 113°–115°.

Test its solubility in various solvents.

Boil 0.1 gm. of acetanilid with 5 cc. of sodium hydroxide T.S. The odor of aniline is noticeable. To the mixture, under a hood, add 0.5 cc. of chloroform and again heat. Note the characteristic and disagreeable odor of phenylisocyanide. (Care!)

Boil 0.1 gm. of acetanilid with 2 cc. of hydrochloric acid until a clear solution results. Add 3 cc. of a 5 per cent solution of phenol in water, followed by 5 cc. of a saturated solution of chlorinated lime. A brownish-red color is produced. Add an excess of ammonium hydroxide. A deep blue color results.

To 0.1 gm. of acetanilid dissolved in 5 cc. of warm water add bromine water, drop by drop, with shaking until the solution remains permanently yellow. A white crystalline precipitate is produced.

Acetphenetidin.—Melting point, 134°–135°.

Test its solubility in various solvents.

Boil 0.1 gm. of acetphenetidin with 3 cc. of dilute nitric acid for 1 minute. Yellow nitroacetphenetidin is formed, and will crystallize in needles.

To 5 cc. of a warm saturated aqueous solution of acetphenetidin add bromine water drop by drop with shaking until a yellow color is obtained. No turbidity or precipitation is produced.

Boil 0.1 gm. of acetphenetidin for 1 minute with 1 cc. of hydrochloric acid, dilute with 10 cc. of distilled water, cool, filter, and add a drop of 10 per cent solution of potassium dichromate to the filtrate. A ruby-red color results.

Antipyrine.—Melting point, 111°–113°.

[illegible] →

Test its solubility in various solvents.

To 2 cc. of an aqueous solution of antipyrine add a few drops of an aqueous solution of tannic acid. A copious white precipitate is produced.

To 2 cc. of a very dilute water solution of antipyrine add 1 drop of ferric chloride solution. A deep red color is produced. Add 0.5 cc. of concentrated sulphuric acid. The color changes to light yellow.

To 10 cc. of a 1 per cent aqueous solution of antipyrine add 0.1 gm. of sodium nitrite. The mixture is almost colorless. Add 1 cc. of dilute sulphuric acid. The deep green color of isonitrosoantipyrine is observed.

↑↑ ↑ May or may not be poisonous

14 Antipyrine

[illegible] will [illegible]

CHAPTER XVI

DIAZOTIZATION. PHENOLS AND RELATED COMPOUNDS

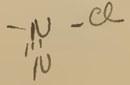
92. Diazotization of Aniline Hydrochloride.—(Text, p. 326.) Mix 30 cc. of water with 25 cc. of concentrated hydrochloric acid in a beaker, and add to the mixture 10 cc. of freshly distilled aniline. Mix well. Aniline hydrochloride is formed. Equation.

Cool the mixture to 0°–5° in ice water. Add 0.5 cc. at a time with constant stirring and without allowing the temperature of the mixture to rise above 5°, a slight excess of a solution of 10 gm. of sodium nitrite dissolved in 30 cc. of water. When about 20 cc. of the nitrite solution has been added, test the mixture for the presence of free nitrous acid by putting a drop of the well-stirred mixture on a piece of iodo-starch paper. A blue color indicates that free nitrous acid is present.

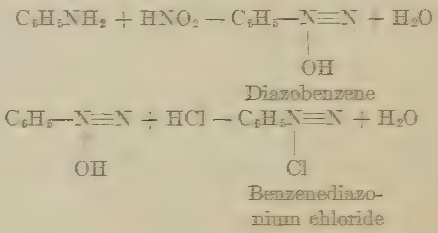
Continue the addition of the nitrite solution until the iodo-starch paper turns a pale but distinct blue immediately upon the application of a drop of the reaction mixture. When this point has been reached, allow the mixture to stand for a few minutes, and repeat the iodo-starch paper test. The apparent excess of nitrous acid noted the first time may have entered into combination making it necessary to add more sodium nitrite. Avoid any considerable excess of sodium nitrite. The solution now contains benzenediazonium chloride (phenyldiazonium chloride). It is to be used in the preparation of phenol in the following exercise.

Note.—The following equations represent the reactions taking place in the preceding exercise:

$$\begin{aligned} &NaNO_2 + HCl \rightarrow NaCl + HNO_2 \\ &C_6H_5NH_2 + HCl \rightarrow C_6H_5NH_2HCl \\ &C_6H_5NH_2HCl + HNO_2 \rightarrow C_6H_5N_2Cl + 2H_2O \end{aligned}$$



Expressed in another way:



$$C_6H_5NH_2 + HNO_2 \rightarrow C_6H_5{-}\underset{\substack{|\\ OH}}{N}{\equiv}N + H_2O$$

$$C_6H_5{-}\underset{\substack{|\\ OH}}{N}{\equiv}N + HCl \rightarrow C_6H_5\underset{\substack{|\\ Cl}}{N}{\equiv}N + H_2O$$

To make iodo-starch paper, dip pieces of filter paper in starch paste containing a small amount of potassium iodide, and dry. The paper must be carefully prepared, and preserved out of contact with acid vapors. It must be handled with clean hands.

When a mixture containing nitrous acid is placed in contact with iodo-starch paper, the following changes take place:

$$KI + HCl \rightarrow KCl + HI$$
$$2HI + 2HNO_2 \rightarrow 2H_2O + 2NO + I_2$$

93. Phenol. Preparation.—(Text, p. 332.) Transfer the solution of benzenediazonium chloride prepared in the preceding exercise, to a flask and heat on a water bath under a reflux condenser at 50° for about 30 minutes. The diazonium compound is hydrolized. Equation. (Write the equation graphically.) Notice any change in odor. (Caution.) Observe any evolution of gas. Arrange for distillation with steam, and distil as long as a few drops of the last portion of the distillate give a color with ferric chloride solution.

Extract the phenol from the distillate by shaking in a separatory funnel with separate small portions of ether, (Care!) after the distillate has been saturated with sodium chloride to reduce the solubility of the phenol in the watery mixture. Filter the combined ether solutions if necessary, and allow the ether to evaporate. Keep the solution away from flames. A residue of phenol is left.

Caution.—Phenol is a dangerous caustic. Its vapor is poisonous and inflammable. Do not inhale. Use alcohol as an antidote if phenol comes in contact with the skin.

Identify phenol in the residue by several of the identification tests described below.

Deportment.—Use pure phenol obtained from the stock room for the following tests.

1. *Physical Properties.*—Observe general appearance; odor; reaction to litmus; and solubility in water, alcohol, glycerin, and sodium hydroxide T.S.

2. *Reaction with Ferric Chloride.*—To 1 cc. of an aqueous solution of phenol add 1 drop of a solution of ferric chloride. Result? This test distinguishes phenol from creosote.

3. *Albumin Test.*—To 2 cc. of an aqueous solution of phenol add 2 cc. of a water solution of albumin. Result? This test distinguishes phenol from creosote.

4. *Collodion Test.*—To 2 cc. of an aqueous phenol solution add 2 cc. of collodion. Result? This test distinguishes phenol from creosote.

5. *Reaction with Bromine.*—To 2 cc. of an aqueous solution of phenol add bromine water, at first slowly and with shaking, and finally in excess. Result?

6. *Reaction with Methenamine.*—Mix 2 gm. of phenol crystals with 0.5 gm. of methenamine in a test tube. Warm until the reaction starts, and then withdraw the heat. The reaction should proceed vigorously. Cool slowly. Observe the properties and solubilites of the resin-like substance formed.

94. Phenylhydrazine Hydrochloride. Preparation. (Text, p. 328. **Caution.**—Do not allow phenylhydrazine hydrochloride to come in contact with the skin.

A. Diazotize the aniline hydrochloride prepared from 5 cc. of freshly distilled aniline in the manner described on p. 87.

B. Dissolve 30 gm. of stannous chloride in 25 cc. of concentrated hydrochloric acid, cool by flowing cold water over the container, and pour the mixture into the solution of the diazo compound (A), slowly and with stirring.

After allowing the mixture to stand for one-half hour or more, filter off the crystals of phenylhydrazine hydrochloride using a Buchner funnel, wash with diluted hydrochloric acid, and dry at room temperature. Turn in the crystals at the stock room.

95. Picric Acid. PREPARATION. (Text, p. 337.) **Caution.**—Picric acid stains the skin. Phenol causes painful burns. Picric acid explodes when heated rapidly or when subjected to percussion.

Mix 5 gm. of concentrated sulphuric acid with 3 gm. of phenol, and heat on a water bath until a clear solution of phenolsulphonic acid is obtained. Equation. Cool. Dilute carefully with an equal quantity of water and pour the mixture slowly and with stirring into 10 cc. of concentrated nitric acid. Equation. Heat on a water bath for 30 minutes, shaking occasionally. Then pour the mixture into 150 cc. of cold water. Filter, and wash the crystals with cold water. Dry at room temperature.

DEPORTMENT. 1. *Solubility.*—Test the solubility of picric acid in water, alcohol, benzin, and dilute ammonium hydroxide. Do the solutions vary in color? Explain. Pour the benzin solution into water. Explain.

2. *Albumin Test.*—To 2 cc. of an aqueous solution of albumin add 2 cc. of a water solution of picric acid. Result?

3. *Alkaloid Test.*—To 2 cc. of an aqueous solution of quinine sulphate add 2 cc. of a water solution of picric acid. Result?

4. *Dyeing Test.*—Soak strips of cotton, woolen, and silk cloths in a hot aqueous solution of picric acid for 15 minutes. Rinse the cloths thoroughly in running water. Is picric acid a dye? If so, for what kinds of fiber?

Caution.—Thoroughly clean the apparatus used in the preceding experiments before storing it in your locker.

96. Cresols. DEPORTMENT. (Text, p. 341.) **Caution.**—Do not allow cresols to touch the skin.

1. *Identification.*—Note the color; odor; density; and solubility in water, alcohol, ether, benzin, and sodium hydroxide T.S. of the cresols supplied.

2. *Reaction with Ferric Chloride.*—To a saturated aqueous solution of cresol add a few drops of a dilute solution of ferric chloride. Result?

3. *Preparation of "Liquor Cresolis Compositus,"* U.S.P.—Mix 35 cc. of linseed oil with 50 cc. of cresol. Add 1.5 gm. of potassium hydroxide and 4 gm. of sodium hydroxide dissolved in 5 cc. of water. Mix well. Heat to about 70° until a portion gives

C_6H_4 HOH_2

a clear solution when mixed with 9 volumes of cold water. Cool the mixture, and add sufficient water to make the product measure 100 cc.

This solution, largely diluted with water, makes an excellent antiseptic and disinfectant.

di-hydroxy-benzene

97. Resorcinol. DEPORTMENT. (Text, p. 344.) 1. *Physical Properties.*—Observe the general appearance; color; odor; and solubility in water, alcohol, benzin, and sodium hydroxide T.S.

2. *Reaction with Ferric Chloride.*—To 2 cc. of a water solution of resorcinol add 3 drops of a dilute solution of ferric chloride. Result?

3. *Reducing Action.*—To 2 cc. of an alkaline solution of silver nitrate add 2 cc. of an aqueous solution of resorcinol. Is there evidence of reduction?

Di-thymol diiodide U.S.P.

98. Thymol Iodide. PREPARATION.—(Text, p. 343.) Dissolve 4 gm. of sodium hydroxide and 3 gm. of thymol in 75 cc. of water. To 75 cc. of water in another container add 20 gm. of potassium iodide and 15 gm. of iodine. Cool the solutions to 0°–10°, and pour the iodine solution slowly, with constant stirring into the thymol solution. Thymol iodide is precipitated. Filter, wash with water until the washings are no longer alkaline to litmus, and dry at 40°–45°. Weigh, and turn in the "aristol" at the stock room. = composition is varied

– $[(C_6H_2 CH_3 C_3H_7 . OI)_2]$

Pyrogallol

1/4 – 1/5 – 1/6 –

Thymol – $C_6H_3(OH)CH(CH_3)_2 CH_3$

Para iso propyl-meta-cresol

CHAPTER XVII

AROMATIC ALDEHYDES AND ACIDS

99. Benzaldehyde. Benzoic Acid. Preparation.—(Text, pp. 352, 360.) Into a round-bottom or Erlenmeyer flask put 15 gm. of benzyl chloride, 125 cc. of water, and 15 gm. of cupric nitrate which is to act as a gentle oxidizer. Add some pieces of pumice to lessen bumping, connect the flask with a water reflux condenser, and boil on a sand bath for 4 hours. Equation.

After refluxing, distil the reaction mixture with steam, continuing the distillation until crystals of benzoic acid are deposited in the condenser. Save the material left in the reaction flask. Separate the benzaldehyde from the water in the distillate by using a separatory funnel, dry over calcium chloride, and redistil, using an air condenser. Reserve that portion of the distillate which comes over at 175°–180°.

Concentrate the solution in the distilling flask from which the benzaldehyde was removed by steam distillation, and set it aside so that benzoic acid may crystallize out. Filter off the crystals, wash with cold water until no copper salt is left, and recrystallize from hot water.

Deportment of Benzaldehyde. 1. *Physical Properties.*—Observe color; odor; density, and solubility in water, alcohol, ether, and benzin.

2. *Spontaneous Oxidation.*—Allow a few drops of benzaldehyde to stand exposed to the air on a watch glass for some time. Observe the formation of crystals. Equation.

3. *Reducing Action.*—Test a solution of benzaldehyde with the Fehling, Schiff, and Tollen tests for the aldehyde group. Is the presence of such a group indicated? Do not be too hasty in making your decision.

4. *Reaction with Sodium Hydroxide.*—Determine if aldehyde resins are formed by the action of sodium hydroxide on benzaldehyde. Compare with formaldehyde and acetaldehyde.

5. *Reaction with Sodium Bisulphite.*—To 1 cc. of benzaldehyde add 5 cc. of a saturated aqueous solution of sodium bisulphite. Shake well. Note the formation of crystals. Equation.

100. Benzyl Alcohol. Benzoic Acid. PREPARATION.—(Text, pp. 349, 360.) To 10 gm. of benzaldehyde add 20 gm. of sodium hydroxide dissolved in 15 cc. of water. Shake thoroughly to form an emulsion, and allow the mixture to stand for 24 hours. One-half of the benzaldehyde is oxidized to benzoic acid; the other half is reduced to benzyl alcohol. Equation. This simultaneous oxidation and reduction is characteristic of the action of caustic alkalies on aromatic aldehydes.

Dissolve the crystalline mass of sodium benzoate in the smallest possible quantity of warm water, and extract the benzyl alcohol from the solution by shaking it with ether. Allow the ether to evaporate spontaneously. An impure benzyl alcohol is left.

Obtain the benzoic acid which remains as sodium benzoate in the water solution in the separatory funnel, by acidifying with hydrochloric acid, filtering, washing with cold water, and purifying by recrystallization. The acid will be oily while hot, and crystalline when cold.

Deportment of Benzoic Acid. 1. *Physical Properties.*—Note the general appearance; odor; reaction to litmus; and solubility in water, alcohol, ether, and benzin.

2. *Effect of Heat.*—Using a small portion in a test tube, heat very gently at first and then with higher heat. Result?

3. *Reaction with Soda-lime.*—Mix 0.5 gm. of benzoic acid with 5 gm. of soda-lime, and heat in a test tube. Note the odor, and the condensation of a liquid on the cool portions of the tube. Equation. **Caution.** Flames!

4. *Reaction with Ferric Salts.*—To a water solution of benzoic acid add 2 drops of a solution of ferric chloride. Result?

5. *Ester Formation.*—Heat in a test tube 2 cc. of methanol, 2 cc. of concentrated sulphuric acid, and 0.5 gm. of benzoic acid. Equation. Pour into 50 cc. of cold water. Observe the odor.

6. *Detection in Foods.*—To 10 cc. of ketchup or other food material add 75 cc. of a saturated water solution of sodium chloride. Make the mixture slightly alkaline with sodium hydroxide T.S. Shake well and allow the mixture to stand for at least an

hour. Shake occasionally. Filter. To the filtrate add a slight excess of hydrochloric acid, and extract it in a separatory funnel with two portions of 10 cc. each of chloroform. Draw off the chloroform, filter if necessary, and allow the chloroform to evaporate spontaneously.

Dissolve a portion of the dry residue in dilute ammonium hydroxide, and evaporate on a water bath until the reaction is neutral to litmus paper. Add 1 cc. of warm water, filter, and add a drop or two of a neutral solution of ferric chloride. If a flesh-colored precipitate of ferric benzoate is produced, the presence of benzoic acid or benzoates in the food is indicated.

101. Salicylic Acid. PREPARATION.—(Text, p. 368.) Boil 5 cc. of methyl salicylate with 15 gm. of sodium hydroxide dissolved in 100 cc. of water, under a reflux condenser until an oily layer is no longer seen, and the odor of methyl salicylate has disappeared. Equation. Cool, and acidulate with hydrochloric acid. Equation. Filter, and wash the crystals with a small amount of cold water. Recrystallize, if desired, by dissolving the crystals in a small amount of warm alcohol and pouring the solution into a considerable quantity of cold water.

DEPORTMENT. 1. *Physical Properties.*—Note the appearance color; reaction to litmus; and solubility in water, alcohol, ether, and benzin.

2. *Reaction with Ferric Chloride.*—To a dilute water solution of salicylic acid add 2 drops of ferric chloride solution. Result?

3. *Ester Formation.*—Heat in a test tube 2 cc. of methanol, 2 cc. of concentrated sulphuric acid, and 0.5 gm. of salicylic acid. Equation. Observe the odor, after pouring the reaction mixture into 100 cc. of cold water.

alol

102. Phenyl Salicylate. PREPARATION.—(Text, p. 371.) Put 2 gm. of salicylic acid in a dry test tube that has been fitted with a glass tube about 45 cm. long which is to act as an air condenser. Heat slowly until the acid melts, and then increase the heat until the acid boils. Continue to boil for 10 minutes. Cool somewhat, and pour the still warm liquid into an excess of cold water in a beaker. Collect the precipitated material and put it in 15–20 cc. of hot water. The phenyl salicylate melts and sinks to the bot-

mol q acid loses CO_2 -- form Salol

tom. Pour off and discard the water, wash the "salol" with another portion of boiling hot water, and then allow it to solidify. Some unchanged salicylic acid may be present.

Deportment. 1. *Physical Properties.*—Observe general appearance; color; odor; and solubility in water, alcohol, and ether.

2. *Reaction with Ferric Chloride.*—To a small amount of an alcoholic solution of phenyl salicylate add a few drops of ferric chloride solution. Result? — dark violet blue color

3. *Identification.*—Heat 0.3 gm. of salol with 3 cc. of sodium hydroxide T.S. for 10 minutes. Equation. Acidify with hydrochloric acid. Equation. Salicylic acid, which can be identified by the usual tests, separates, and the odor of phenol is recognized.

103. Aspirin. Preparation.—(Text, p. 372.) In a small flask or large test tube fitted with a reflux condenser mix 5 gm. of salicylic acid, and 5 gm. of acetic anhydride. (Care!) Add 0.5 cc. of concentrated sulphuric acid and heat the mixture on a water bath for 30 minutes, keeping the temperature of the reaction mixture between 60° and 80°. Equation. Remove the condenser, and allow the mixture to cool. Stir occasionally. The aspirin settles out. Filter, and discard the filtrate. Recrystallize the acetylsalicylic acid from warm alcohol, avoiding high temperatures which favor the formation of salicylosalicylic acid.

Avoid contact with iron utensils during this experiment, for iron acts catalytically to form compounds in which the acetyl group enters the nucleus.

Deportment. 1. *Physical Properties.*—Note general appearance; taste; odor; and solubilities.

2. *Reaction with Ferric Chloride.*—Apply the ferric chloride test for salicylic acid to a water solution of aspirin. Result?

3. *Hydrolysis.*—Boil 0.3 gm. of aspirin with 10 cc. of water for several minutes. Equation. Cool, filter, and add a drop or two of ferric chloride solution. The presence of a violet-red color indicates that hydrolysis has taken place. Why? Equation.

4. *Saponification.*—Boil 0.5 gm. of aspirin with 10 cc. of sodium hydroxide T.S. for 10 minutes. Equation. Cool, and add an

excess of sulphuric acid. Equation. A white precipitate of salicylic acid should be seen, and the odor of acetic acid should be perceptible.

104. Gallic Acid. DEPORTMENT. (Text, p. 373.) 1. *Physical Properties.*—Note general appearance; color; odor; and solubility in water, alcohol, ether, and chloroform.

2. *Reducing Action.*—To 5 cc. of Fehling's solution add 1 cc. of a 10 per cent water solution of gallic acid. Boil. Result?

3. *Reaction with Ferrous Salts.*—To 2 cc. of an aqueous solution of gallic acid add 2 cc. of a freshly prepared aqueous solution of pure ferrous sulphate. Result?

4. *Reaction with Ferric Salts.*—To 2 cc. of an aqueous solution of gallic acid add a few drops of a neutral solution of ferric chloride. Result?

5. *Effect on Gelatin.*—To a water solution of gelatin add an equal amount of a 10 per cent aqueous solution of gallic acid. Result?

6. *Ink.*—To 0.5 gm. of gallic acid dissolved in 5 cc. of hot water, add 5 cc. of a freshly prepared 5 per cent solution of ferrous sulphate, made from clear green crystals from which any brown ferric salt has been removed. Mix well. Using a clean pen point write with the solution on a piece of paper.

To one-half of the solution add a small amount of neutral ferric chloride solution. Write with this solution on another piece of paper. Set both papers aside until the next exercise. Compare, and explain.

105. Tannic Acid. DEPORTMENT. (Text, p. 375.) 1. *Physical Properties.*—Observe general appearance; color; odor; and solubility in water, alcohol, ether, and chloroform.

2, 3, 4, 5. Perform tests Nos. 2–5 as described under Gallic Acid, using tannic acid in each case instead of gallic acid.

6. *Effect on Alkaloids.*—To 2 cc. of a dilute solution of quinine sulphate or other alkaloidal salt, add 1 cc. of an aqueous solution of tannic acid. Result?

7. *Ink.*—Prepare ink as described under Gallic Acid, using tannic acid instead of gallic acid. Results?

8. *Tannin in Tea.*—Upon 1 gm. of tea pour 10 cc. of boiling water. Allow to stand for 10 minutes. Pour off about 2 cc.

of the infusion and to it add a few drops of ferric chloride solution. Result?

Heat the rest of the infusion with the tea leaves to boiling, and boil for 5 minutes. Cool, and to 2 cc. of the clear liquid add a few drops of ferric chloride solution. Result? What objection is there to making tea by boiling?

CHAPTER XVIII

ALKALOIDS

17-3'

106. Precipitation Tests.—(Text, p. 414.) Use separate 2 cc. portions of an aqueous solution of quinine sulphate or other alkaloidal salt for each of the following tests. Add a few drops of the reagent at first, shake, and continue to add the reagent until at least 2 cc. has been added. Note the results obtained upon the first addition of the reagent, and when the reagent is in excess.

General Alkaloidal Reagents.

1. Mayer's reagent, (mercuric-potassium iodide).
2. Mercuric chloride.
3. Tannic acid.
4. Picric acid.
5. Phosphomolybdic acid.
6. Iodine, in aqueous solution.

A positive test obtained with any or all of these reagents merely indicates the presence of an alkaloid; it does not identify the alkaloid. Some of the reagents give characteristic reactions with any amine. Therefore the formation of a precipitate is not always conclusive evidence of the presence of an alkaloid. (amine)

ead

107. Extraction of a Volatile Alkaloid.—Boil together in a distilling flask for 15 minutes 25 cc. of water, 5 cc. of dilute sulphuric acid, and 2–4 gm. of tobacco. After boiling, make the solution slightly alkaline with sodium hydroxide T.S., and distil until 10 cc. of distillate has been obtained. Test separate portions of the well mixed distillate with Mayer's reagent, tannic acid, iodine, and the other alkaloidal precipitants in order to demonstrate the presence of an alkaloid in the distillate.

Read

108. Extraction of a Non-volatile Alkaloid.—Gently heat 3 gm. of ground cinchona bark for 15 minutes with 20 cc. of water and

Amine also gives test with

5 cc. of dilute sulphuric acid. Filter. Cool. Place in a separatory funnel and add 15 cc. of ether, 5 cc. of chloroform, and enough sodium hydroxide T.S. to give a marked alkaline reaction. Shake occasionally during 15 minutes. Discard the aqueous liquid, and shake the ether-chloroform mixture with 10 cc. of water mixed with 5 cc. of dilute sulphuric acid. Make sure that the reaction is acid. Draw off the acid liquid through a filter paper and test separate portions of it for the presence of alkaloids by the usual precipitation tests.

109. Identification Tests.—The following table shows some of the color reactions of a few of the alkaloids. Additional identification tests for these alkaloids and for a number of other alkaloids will be found in the *United States Pharmacopoeia, X*; Allen's *Commercial Organic Analysis*, and other reference books.

Perform the tests by placing a very small amount of the pure alkaloid or alkaloidal salt on a porcelain color plate or on a watch glass set on a piece of white paper, adding a single drop of the reagent, and stirring with a clean glass rod. If a solid reagent is used, draw a crystal of it through the mixture with a clean glass rod. Observe all color changes carefully, for the colors are often fugitive and vary somewhat with the conditions of the test. Since the colors are often modified by the presence of impurities, the tests should be performed upon fairly pure samples.

When an idea has been gained as to the identity of the alkaloid, use special confirmatory tests to justify your conclusion. Then obtain a sample of the pure alkaloid and make comparative tests. The work requires much skill and patience. Do not become discouraged. Much experience and practice are necessary to make one expert at the work.

The blanks in the following table indicate that no characteristic color reactions are produced.

110.

COLOR REACTIONS OF CERTAIN ALKALOIDS

Reagents	Morphine	Codeine	Quinine	Strychnine	Brucine
Conc. C. P. H_2SO_4.	Pale red or yellowish. Brown if heated.	Reddish to violet, red on warming	Colorless, to light yellow.	Colorless to pale yellow.	Pale rose.
Conc. C. P. H_2SO_4 with $K_2Cr_2O_7$.	Brown.	Olive.	Yellow.	Blue to violet, to red, to orange or yellow.	Orange.
Conc. C. P. H_2SO_4 with H_2MoO_4.	Purple to blue.	Yellowish to green, to blue.	Greenish.		Orange to red.
Conc. C. P. H_2SO_4 with a crystal of KNO_3.	Rose red to brown if heated.	Blue to brown.			Reddish.
Conc. C. P. HNO_3.	Orange-red, fading to yellow.	Orange-red.			Blood red.

111. Special Tests for Certain Alkaloids. Brucine.—To a small portion of the alkaloid add a drop of concentrated sulphuric acid and a small crystal of potassium nitrate. A reddish or brownish-red color is produced. Heat on a steam bath until the color fades to yellow. Add 1 drop of a 10 per cent solution of stannous chloride. A purple color is produced.

Caffeine.—For caffeine tests, see p. 77.

Cocaine.—The tests are usually performed upon the hydrochloride, first making it if necessary.

(a) To 5 cc. of a 2 per cent solution of cocaine hydrochloride add 5 drops of a 5 per cent solution of chromium trioxide. A yellow precipitate is formed, but it dissolves when the mixture is shaken. Add 1 cc. of hydrochloric acid. A permanent orange-colored precipitate is formed.

(b) Mix a small quantity of cocaine hydrochloride with an equal amount of dry mercurous chloride on a porcelain surface. Breathe upon it. A black color is produced.

(c) To 2 drops of a dilute solution of cocaine hydrochloride add 1 cc. of a 3 per cent solution of potassium permanganate. A violet precipitate, which appears brownish-violet when collected upon a filter paper, is produced.

(d) Heat 0.1 gm. of cocaine with 1 cc. of sulphuric acid at 100° for 5 minutes. Then cautiously mix with 2 cc. of distilled water. The odor of methyl benzoate is noticeable, and upon cooling, crystals of benzoic acid separate.

Codeine.—(a) Warm a small amount of codeine in a porcelain dish with a drop or two of sulphuric acid and add a drop of a solution of formaldehyde. A light-blue color is produced.

Know

(b) To 0.01 gm. of codeine dissolved in 5 cc. of sulphuric acid add 1 drop of a solution of ferric chloride. The solution becomes blue when warmed, and changes to red on the further addition of a drop of nitric acid.

(c) To 0.01 gm. of codeine add a few drops of sulphuric acid containing 0.005 gm. of selenious acid in each cc. A green color is produced, which changes rapidly to blue, then slowly back to grass-green.

Morphine.—Morphine is unusual in that it does not dissolve freely in either chloroform or ether. Hot amyl alcohol is a good solvent for this alkaloid. Exceptional others do

(a) To a solution of a morphine salt add a few drops of a dilute solution of potassium ferricyanide to which has been added a small amount of ferric chloride. A deep blue color is produced at once. On standing a blue precipitate separates.

(b) To a solution of a morphine salt add a few drops of sulphuric acid containing a small amount of formaldehyde. An intense purple color is produced.

(c) To a solution of morphine sulphate add a few drops of sulphuric acid containing 0.005 gm. of selenious acid in each cc. A blue color is produced which changes to green and then to brown.

Quinine.—(a) A solution of quinine in dilute sulphuric acid exhibits fluorescence when examined in a strong light over a black surface. The fluorescence is destroyed by hydrochloric acid or chlorides. It is brought back by the addition of more sulphuric acid.

(b) To 5 cc. of a saturated aqueous solution of quinine add 3–5 drops of bromine water followed by 1 cc. of ammonium hydroxide. An emerald green color is produced by the formation of thalleoquin. If neutralized by an acid, the color changes to blue. When further acidified, the blue color changes to red.

Strychnine.—(a) To a small amount of strychnine add a few drops of sulphuric acid containing 1 per cent of ammonium vanadate. A deep violet-blue color, changing to a deep purple, and finally to a cherry red, is produced.

(b) Heat a small amount of strychine nitrate with a few drops of hydrochloric acid. A bright red color is produced.

112. Identification of Single Alkaloids.—Obtain several "unknown" samples of alkaloids at the stock room and identify each. In reporting each sample indicate the tests upon which your conclusions are based.

113. Examination of Organic Matter for Certain Alkaloids.—"Stomach contents" consisting of minced meat or cracker crumbs mixed with one or two alkaloids is furnished. Proceed to extract the alkaloids as follows:

1. Dissolve or extract the finely-divided material with 5–10 times its volume of 0.1 per cent hydrochloric acid at 50° for several hours or over night. Strain off the liquid and filter it. Evaporate on a steam bath to a small volume, and then add 5 times its volume of alcohol. Allow the mixture to stand at room temperature for several hours, with occasional shaking, and filter. Add 15 cc. of water and drive off the alcohol by evaporating on a steam bath until the volume measures about 25 cc. Filter if necessary. The filtrate contains the alkaloids in the form of the chloride or hydrochloride. The solution must be acid in reaction at this point.

2. Extract the alkaloids as follows:

A. Extract the alkaloidal solution in a separatory funnel with petroleum benzin. This solvent removes fats which will form emulsions and cause difficulties in making separations if allowed to remain in the solution.

B. Extract the acid solution from A with benzene. Caffeine will be removed.

3. Make the acid solution from B slightly alkaline by adding ammonium hydroxide, testing with litmus paper. If any considerable amounts of alkaloids are present, the alkaloids will be precipitated at this point. Do not filter if precipitation occurs.

C. Extract the alkaline solution with petroleum benzin. Quinine, nicotine, and veratrine, with traces of strychnine and cocaine will be found in the benzin.

D. Extract the alkaline solution from C with benzene. Cocaine, strychnine, codeine, and atropine may be found in the benzene solution.

E. Extract the alkaline solution from D with chloroform. Cinchonine and cinchonidine, with traces of morphine will be found in this solution.

F. Extract the alkaline solution from E with amyl alcohol. Morphine will be dissolved by the amyl alcohol.

In performing the extractions, care must be taken to obtain the complete removal of all the alkaloids of a group before passing on to the next group. Violent mixing is to be avoided. More complete removal of the alkaloids of a group is obtained by the use of several extractions, using a small portion of fresh solvent each time, than by a single extraction using the same total amount of solvent.

Evaporate a few drops of the immiscible solvent from each extraction on watch glasses to determine if any substance has been extracted. Dissolve small portions of any residue obtained in a drop of 0.1 per cent hydrochloric acid, and make suitable tests to determine the identity of the alkaloid.

Caffeine, codeine, cocaine, morphine, quinine, and strychnine may be found in the material furnished. Two alkaloids which would be dissolved by the same solvent in the process of extraction, will not be found in the "unknown" samples furnished at the stock room.

The extraction method described above is based on that of Dragendorff. The Stas-Otto and the Kippenberger processes are exceedingly useful.

114. Examination of Tablets for Alkaloids.—Make an acid-water solution of a pill or tablet, filtering off any insoluble matter, and test with the general alkaloidal precipitants to determine if any alkaloid is present.

If the preliminary test shows the presence of an alkaloid, grind the pills or tablets to a fine powder, extract them with warm 95 per cent alcohol, filter, and evaporate the filtrate nearly to dryness. Treat the residue with dilute sulphuric acid, dilute with warm water, and filter the solution into a separatory funnel. Extract with the several immiscible solvents as directed in Exercise **113,** and identify the alkaloid.

Several alkaloids are not usually found in the same material. Commonly only one, or seldom more than two are found, even in medicinal preparations. If many alkaloids are found together, their separation may be extremely difficult or almost impossible.

Alkaloids - important principle of plant
- + treated c acid media
-- not sol in H_2O - sol alcohol
salts " " " not " "

Solid or Liquid

ef.-
scuss general characteristics
l. - of salts & alkaloid
ethods of extraction
ests for solution of
annic acid used in tests?
what form do alkaloids occur in plants
(quinic acid / (meconic acid)
wo main groups - Groups

CHAPTER XIX

COAL-TAR COLORS

115. Detection of Coal-tar Colors.—(Text, p. 435 *et seq.*) Dissolve some highly colored cheap candy in water, put a piece of clean white woolen cloth in the solution and boil for 10 minutes. Remove the cloth and rinse it well in hot water. If the cloth remains brightly colored, dyes or coloring matters are present.

Boil the colored cloth in a dilute solution of ammonium hydroxide. The coloring matter dissolves, and if coal-tar colors are present the resulting solution usually has a blue or purplish color. To the ammoniacal solution add hydrochloric acid until there is a slight acid reaction. Immerse a fresh piece of white woolen cloth in the solution, and boil. Rinse the cloth well with hot water. If the cloth remains colored, the presence of coal-tar dyes is proved.

116. Testing Butter for Artificial Color.—(Text, p. 446.) Shake 4 gm. of butter or oleomargarine in a separatory funnel with a mixture of 4 cc. of carbon disulphide and 20 cc. of alcohol. Allow the mixture to stand until a good separation into layers is obtained. The lower carbon disulphide layer contains the fat; the upper alcoholic layer contains the coloring matter. Separate the two layers and test the alcoholic solution as follows: Add 15 cc. of water, acidify slightly with hydrochloric acid, put in it a small piece of white woolen cloth, and boil for 10 minutes. Remove the cloth and rinse it well in boiling water. Strip the color from the cloth by boiling it for a few minutes in a dilute solution of ammonium hydroxide. Remove the cloth, add dilute hydrochloric acid to the ammoniacal solution until the reaction is faintly acid, and then boil in it for ten minutes a new piece of white woolen cloth. If the second piece of cloth is permanently stained, and the color cannot be removed by boiling it in hot water, a coal-tar dye was present in the material examined.

117. Phenolphthalein.—(Text, pp. 378, 445). Mix in a dry test tube 0.5 gm. of phthalic anhydride, 0.5 gm. of phenol, and 0.5 cc. of concentrated sulphuric acid. Heat to about 160° for 5 minutes. Cool. Carefully dilute with 10 cc. of water and make the solution slightly alkaline by adding sodium hydroxide T.S. slowly, and with stirring. Observe the color of the solution. Pour the mixture into an excess of cold water and acidulate with hydrochloric acid. Result? Make alkaline again with sodium hydroxide T.S. Result?

118. Fluorescein. PREPARATION.—(Text, p. 445.) Dehydrate 5 gm. of commercial zinc chloride by melting it in a porcelain dish over a low flame and heating it at low temperature for 10 minutes. To the zinc chloride add 5 gm. of phthalic anhydride and 7 gm. of resorcinol. Mix well. Heat carefully to about 180°–200° for an hour or more, or until the liquid solidifies. Cool, remove the solid mass, and pulverize it in a mortar. Boil with 125 cc. of water and 20 cc. of concentrated hydrochloric acid for 10 minutes. Any of the substances which have not entered into the reaction will be dissolved out, and fluorescein will be left. Filter out the solid fluorescein, wash with water on a filter, and dry. Recrystallize by dissolving in hot alcohol and pouring the solution into an excess of cold water.

DEPORTMENT. 1. *Fluorescence.*—Dissolve a small amount of fluorescein in a dilute solution of sodium hydroxide. Note the color of the solution by reflected and by transmitted light.

2. *Dyeing.*—Determine if fluorescein is a direct dye for cotton, wool, or silk, by boiling clean pieces of white cloth of each kind in a solution of fluorescein dissolved in sodium hydroxide T.S. for at least 10 minutes. Remove the cloths and rinse well in boiling water. Results?

119. Eosin. PREPARATION.—(Text, p. 445.) To 2 gm. of fluorescein and 10 cc. of alcohol contained in an Erlenmeyer flask add slowly, drop by drop from a dropping funnel, 2 cc. of bromine. Shake well. When about one-half the bromine has been added, a clear dark reddish-brown solution is obtained. This marks the formation of the dibrom-substitution product. When all the bromine has been added, the insoluble tetrabrom-derivative is formed and precipitated. Let the mixture stand for one hour. Filter, wash the precipitated tetrabromfluorescein with cold alcohol, and dry. Each molecule of eosin is now combined with one molecule of alcohol. The alcohol can be removed by heating the eosin to 110°.

DEPORTMENT. 1. *Solubilities.*—Determine the solubility of eosin in water, alcohol, and a dilute solution of sodium hydroxide. Examine the colors of the solutions by both reflected and transmitted light.

2. *Dyeing.*—Make a solution of eosin in sodium hydroxide T.S. and test its ability to dye cotton, wool, and silk directly, as described under Fluorescein.

120. Ammonium Salt of Eosin. PREPARATION.—Put 25 cc. of concentrated ammonium hydroxide in an evaporating dish. Over the dish place a triangle which supports a filter paper on which 1–2 gm. of eosin has been spread out. Cover the evaporating dish and eosin with an inverted beaker and allow to stand until the next exercise. Note the change in the color of the eosin.

DEPORTMENT. 1. *Solubility.*—Test the solubility of the ammonium salt of eosin in water.

2. *Red Ink.*—With a new steel pen use some of the water solution as an ink. Result?

Would the use of this solution as a food color be permitted?
Could this water solution be used as rouge?

121. Methyl Orange. PREPARATION.—(Text, p. 447.)

A. Diazotize 5 gm. of sulphanilic acid as follows: In 60 cc. of water dissolve 2 gm. of sodium hydroxide and 5 gm. of sulphanilic acid. The solution must be alkaline. Equation. Cool with ice to 0°–10°. To the solution add 3 gm. of sodium nitrite dissolved in 15 cc. of cold water, and then add slowly with stirring 5 cc. of concentrated hydrochloric acid that has been diluted with 5 cc. of ice water. Equation. Let the solution stand in an ice bath for 30 minutes.

B. In another flask or beaker dissolve 3 cc. of dimethylaniline in a mixture of 10 cc. of water and 5 cc. of concentrated hydrochloric acid. Cool, and add this solution very slowly, with stirring, to (A), the solution of diazotized sulphanilic acid. Equation.

C. To the reddish oily-appearing mass which forms add a cold 25 per cent water solution of sodium hydroxide until the color of the mixture shows that the reaction is just alkaline. Then add to the mixture as much sodium chloride as will dissolve. Heat just to boiling, cool, and filter through two fluted filter papers. Purify by recrystallization from hot water. Dry at room temperature.

Deportment. 1. *Color Changes.*—Dissolve a little methyl orange in water, and alternately add acid and alkali, observing the color changes.

2. *Dyeing.*—Determine if methyl orange is a direct dye for cotton, silk, or wool, by the method employed under Fluorescein.

CHAPTER XX

PROTEINS

Skip

122. Detection of Elements.—(Text, p. 450 *et seq.*) Test small quantities of egg white for the presence of carbon, hydrogen, nitrogen, sulphur, and phosphorus by the methods described in Chapter II.

Use a cold water solution of egg white for the following tests:

123. Precipitation Tests. 1. *Mineral Acids.*—Layer 5 cc. of the protein solution over 5 cc. of concentrated nitric acid in a test tube. Result? Repeat the test using fresh portions of the protein solution and concentrated hydrochloric and sulphuric acids. Results? Perform the same tests using diluted acids in each case. Results? = Ppt

2. *Acetic Acid.*—To a portion of the protein solution add a few drops of glacial acetic acid. Result? How does the action compare with that of mineral acids? — no ppt

3. *Salts of Heavy Metals.*—To 5 cc. of protein solution add 0.5 cc. of a solution of lead subacetate. Result? To a new portion of the protein solution add a few drops of a solution of mercuric chloride. Result? Ppt

Why is white of egg used as an antidote in poisoning by mercury?

To 5 cc. of Fehling's solution add 0.5 cc. of protein solution, and heat. Result?

Can a reducing sugar be determined by the Fehling process when protein is also present?

4. *Alkaloidal Reagents.*—Test separate portions of the protein solution with Mayer's reagent, picric acid, and tannic acid. Results?

124. Coagulation Tests. 1. *Heat.*—Heat 3 cc. of the protein solution to boiling. Does coagulation take place?

2. *Heat and Acetic Acid.*—To 3 cc. of protein solution add 2 drops of dilute acetic acid, and boil. Result? Compare with the preceding test.

3. *Alcohol.*—To 3 cc. of the protein solution add 10 cc. of alcohol and set aside until the next exercise. Result? Test the solubility of the precipitated protein in water. Result?

125. Color Reactions. 1 *Molisch Reaction.*—To 1 cc. of protein solution add 3 drops of a solution of alphanaphthol in chloroform. Mix. Layer the mixture over 5 cc. of concentrated sulphuric acid in a test tube, and allow to stand for a few minutes. Result? This test detects carbohydrate groups.

2. *Biuret Reaction.*—Mix 2 cc. of protein solution with 2 cc. of 10 per cent sodium hydroxide solution, and to the mixture add not more than 2–3 drops of a 0.5 per cent aqueous solution of cupric sulphate. Result?

In performing this test it is well always to use the same amounts of reagents, for variations, especially in the amount of cupric sulphate used, may lead to errors in conclusions. Compounds which respond to this test have at least two —CO—NH— groups.

3. *Millon's Reaction.*—To 2 cc. of protein solution add 4–5 drops of Millon's reagent. Result? Heat to boiling. Result?

Compounds containing phenolic hydroxyl respond to this test.

4. *Xanthoproteic Reaction.*—To 2 cc. of protein solution add 0.5 cc. of concentrated nitric acid, and heat. Result? Note the odor. Cool, and make the solution alkaline with an excess of ammonium hydroxide. Result?

The color is produced by the formation of nitro compounds containing a benzene ring.

5. *Hopkins-Cole Reaction.*—To 2 cc. of protein solution add 0.5 cc. of a solution of glyoxalic acid. Shake. Layer the mixture over 5 cc. of concentrated sulphuric acid. Allow to stand for a few minutes. Result?

This test depends upon the presence of a tryptophan group in the protein.

C H. · H H_2CrO_4

APPENDIX

Reagents.—Unless otherwise specified, test solutions of the composition and strength specified on pages 486–493 of the *United States Pharmacopoeia, X*, are to be used in all exercises.

The composition of a few of the more commonly used reagents is here given.

Alkaline Potassium Permanganate Test Solution.—Use a 0.01 per cent solution of potassium permanganate in 2 per cent aqueous potassium hydroxide solution.

Fuchsin-sulphurous Acid Test Solution. Schiff's Reagent.—Dissolve 0.2 gm. of fuchsin in 120 cc. of hot distilled water, cool, and add a solution of 2 gm. of anhydrous sodium suphite in 20 cc. of distilled water, followed by 2 cc. of concentrated hydrochloric acid. Dilute the solution with distilled water to 200 cc. and allow it to stand for 1 hour before using. This solution does not keep well.

Tollen's Reagent.—Mix equal volumes of (A), a 10 per cent aqueous solution of sodium hydroxide, and (B), a 10 per cent solution of silver nitrate in concentrated ammonium hydroxide diluted with an equal volume of water. Keep the solutions in separate bottles, and mix just before using. Thoroughly clean the apparatus in which tests for aldehydes using this reagent are performed.

Fehling's Solution. Alkaline Cupric Tartrate Test Solution.

A. Dissolve 34.66 gm. of cupric sulphate crystals in enough water to make 500 cc. of solution.

B. Dissolve 173 gm. of potassium and sodium tartrate and 50 gm. of sodium hydroxide in sufficient water to make the solution measure 500 cc.

Keep the solutions in separate bottles. For use, mix equal volumes of the two solutions at the time required.

The sodium and potassium tartrate is here used to prevent the precipitation of cupric hydroxide when the copper and alkaline solutions are mixed. A reducing agent changes the copper from the cupric to the cuprous condition, and precipitates it as red cuprous oxide.

In performing the Fehling test qualitatively, the reagent should always be in excess. If the liquid to be tested is acid in reaction, it should be neutralized before carrying out the test. After mixing, the reagent and the substance to be tested should always be boiled for at least one minute, and allowed to stand until cool if necessary, before reading the result of the test.

Molisch's Reagent.—A 10 per cent solution of alphanaphthol in chloroform.

Benedict's Qualitative Reagent.—Dissolve 173 gm. of sodium citrate and 100 gm. of anhydrous sodium carbonate in about 600 cc. of water. Filter if necessary. In a separate container dissolve 17.3 gm. of crystalline cupric sulphate in 150 cc. of water. Add the copper solution with constant stirring to the citrate-carbonate solution, and dilute to 1000 cc.

Alkaline Sodium Hypobromite Test Solution.—To a solution of 40 gm. of sodium hydroxide in 150 cc. of water, add 10 cc. of bromine. Shake well, and add water to 200 cc. This solution must be freshly prepared when required.

Mayer's Reagent.—Mercuric Potassium Iodide Test Solution. Dissolve 1.358 gm. of mercuric chloride in 60 cc. of water and add 5 gm. of potassium iodide in 10 cc. of water. Mix the two solutions, and add water to 100 cc.

Hopkins-Cole Reagent.—Cover 10 gm. of magnesium with distilled water and slowly add 250 cc. of a saturated aqueous solution of oxalic acid, cooling under the tap. Filter off the insoluble magnesium oxalate. Acidify the filtrate with acetic acid, and dilute with distilled water to make 1000 cc. Keep in a well stoppered bottle with a little chloroform.

Millon's Reagent.—Dissolve 100 gm. of mercury in 142 cc. of concentrated nitric acid. Add 280 cc. of distilled water. Filter if necessary.

Phosphomolybdic Acid Test Solution.—Dissolve 5 gm. of phosphomolybdic acid in 15 cc. of concentrated nitric acid that has been diluted with 35 cc. of water. Filter if necessary.

Phosphotungstic Acid Test Solution.—Use a 2 per cent solution of phosphotungstic acid in a 5 per cent solution of sulphuric acid.

Tannic Acid Test Solution.—Dissolve 1 gm. of tannic acid in 1 cc. of alcohol, and add sufficient water to make 10 cc. Prepare fresh when required for use.

Picric Acid Test Solution.—Use a 1 per cent solution of picric acid in distilled water.

Iodine Test Solution.—Dissolve 0.5 gm. of iodine and 1.5 gm. of potassium iodide in 25 cc. of distilled water.

Schweitzer's Reagent.—Dissolve 10 gm. of ammonium chloride in 250 cc. of N/2 cupric sulphate volumetric solution. Add a solution of sodium hydroxide until precipitation is complete. Filter, wash the precipitated cupric hydroxide with water, and dissolve it in 1 liter of concentrated ammonium hydroxide.

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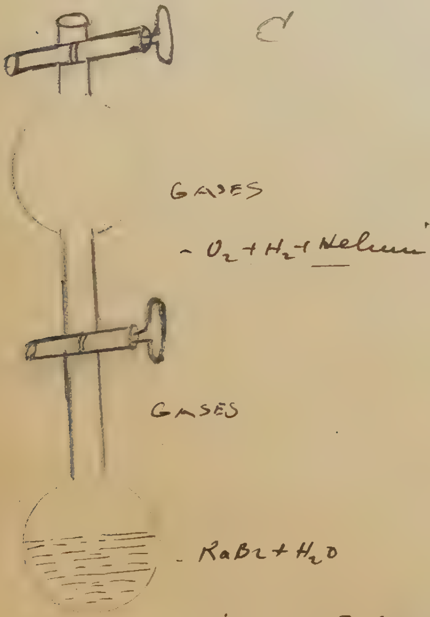
An ordinary piece of metal cons
of a multitude of crystals pointing in al
ways.

By a somewhat complicated process of heating + stretching the many small crystals can be all be made to line up + form a small number of large crystal



EXTRACTION OF GASES FROM RADIUM BROMIDE

lcohols, primary	– $R \cdot CH_2OH$
" , secondary	R_2CHOH
" , tertiary	R_3COH
ldehydes	$RCHO$
Ketones	R_2CO
Acid	$RCOOH$
Esters	$RCOOR$
Ethers	ROR

Interpolation

assay of K_2SO_4

Plunge method

- Rules

- front of Book -

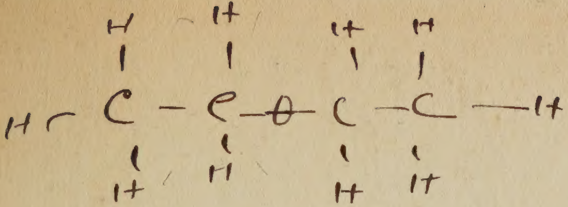
Volumetric & Gravimetric analy

Cerium Oxalate - 3 gr

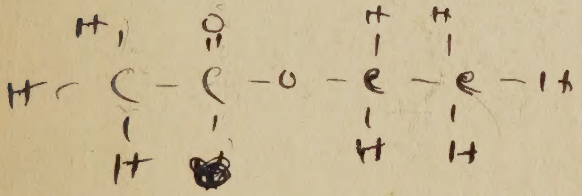
- anti emetic

vomiting ~~[illegible]~~ in pregnancy

N.F.



Ether



Reason

acetic ether

Methyl, Carbonyle acetic ether

$H_3C \cdot CO - O \cdot CH_2CH_3$

$H_3 \cdot CH_2 \cdot O - CH_2 \cdot CH_3$ - Ether

*TW-774-